PASSIVITY OF CHROMIUM[1,2]

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ABSTRACT

Surfaces of chromium, treated with nitric acid and then oxidized in air at various temperatures, were examined by electron diffraction and these results were correlated with results of electrode potential measurements on other samples subjected to the same treatments. The potentials taken at the time of immersion in saturated potassium chloride were found to be a function of the temperature of oxidation with a maximum noble potential corresponding to an invisible oxide film and a minimum corresponding to a surface on which oxide could not be detected. Air-passivation treatment was compared with nitric acid passivation.

The potential was found to be a function of time. As yet no correlation has been noticed between continuation of passivity in the potassium chloride solutions and the temperature of oxidation. However, it was seen that heating above 300°C. caused a more rapid decrease in initial potential than did the lower temperature treatments.

It was concluded that an oxide film is not the fundamental criterion of passivity in the case of chromium; but the presence of such a film can greatly influence the measured potential of the metal.

INTRODUCTION

The phenomenon of passivity has been the subject of study and discussion for some time, with a number of theories being proposed to explain its cause. Since passive metals differ somewhat in behavior, the theories have differed with relation to which metals or alloys were used as examples.

The oxide film theory has been the most generally accepted, especially since Evans (1) succeeded in stripping invisible films from metal surfaces. In the past decade however, a theory based on electronic interaction in alloys and also the formation of chemisorbed films, has been developed (2, 3, 4). This theory has received considerable experimental support in its application to certain alloys. In a still more recent development, Fontana (5) obtained some experimental evidence indicating that physically adsorbed oxygen plays an important part in the cause of passivity of stainless steel.

A number of other workers have contributed evidence for or against the oxide film theory. The literature includes a number of such experiments with chromium. According to Erich Müller (6), the passivity of chromium is explained not on the basis of an oxide film but on the basis of the close-packed array of the metal atoms which can react only after they have been

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loosened on the surface by some external force such as scratching, electrolytic action, or introduction of an impurity. Still another theory (7) attributes stability of the metal to the sharing of electrons of neighboring chromium atoms in the unit cell. However, truly convincing evidence for the cause of passivity of chromium is still lacking.

The purpose of the present research was to accumulate additional information on the passivity of chromium by a combination of techniques, including potential measurements and surface studies by electron diffraction methods.

EXPERIMENTAL

Samples of spectroscopically pure electrolytic chromium, prepared by plating on copper and then stripping off the chromium as described in an earlier work (8), were used throughout this investigation. It was desired to eliminate the basis metal because of the porosity of chromium deposits.

In a preliminary experiment, an attempt was made to strip oxide films from chromium mechanically. A drop of sodium silicate solution was placed on the surface, allowed to solidify, and then pulled off. It was found that films thicker than that producing a first order blue interference color could be pulled off by this method, whereas the thinner films could not. This change in the mechanical properties of the film in the region of the blue color initiated further interest in various thicknesses of the oxide.

One group of samples was left in concentrated nitric acid solution for ten days. This treatment produced a quite noble potential which measured more than +0.8 v. with respect to the saturated calomel electrode. Another group of samples was exposed to air for periods ranging from one to two months. The pieces were then heated in an electric furnace at various temperatures for a period of one hour under atmospheric conditions. They were then cooled and immersed in an aerated solution of saturated potassium chloride at 35°C. Potentials were measured at frequent time intervals using a saturated calomel electrode as reference. Saturated potassium chloride electrolyte was used to eliminate liquid junctions and also because it causes a breakdown of passivity with time, thereby giving a basis for comparison of the effectiveness of different treatments in augmenting or inducing passivity.

Typical time-potential curves for these experiments are given in Fig. 1. These curves were extrapolated to zero time to obtain values for the potentials at the time the metal was initially immersed. Extrapolations were made with little uncertainty in most cases, the exceptions being those for oxidation temperatures of 500 and 600°C. In these cases the potentials dropped quite rapidly at first and the steep slopes of the curves made the extrapolations somewhat uncertain.

Electron diffraction patterns were obtained on pieces of chromium which had been subjected to the same treatments as those used for potential measurements. The patterns were obtained by using the diffraction attachment of an electron microscope.[3] The specimens were mounted in the column of the microscope so that the main surface was almost parallel to the electron beam. By a system of controls the specimens could be tilted, rotated or translated, and were adjusted so that the incident beam

[3] RCA type emu-1.

struck at a low glancing angle, thereby producing reflection patterns. The electrons were accelerated through a 50,000 volt drop which produced a wave length of approximately 0.05 Å.

RESULTS AND DISCUSSION

Table I summarizes the results of potential measurements and electron diffraction studies. The potentials are plotted in Fig. 2 as a function of the temperature to which the pieces were heated. The solid line was obtained using samples from the nitric acid treatment and the dotted line from those treated only in air. A maximum and minimum occur in the curve for the former case, but neither is obtained where air-passivation alone was used.

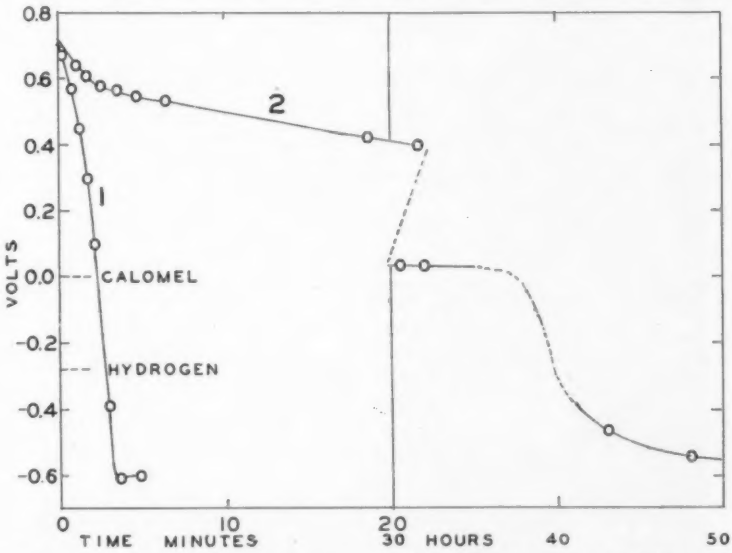

FIG. 1. Typical time-potential curves for chromium in saturated KCl. 1—no HNO_3 treatment, oxidized 1 hr. at 500°C. 2—3 days in HNO_3, no heating.

It should be noted that none of the values on these curves would correspond to the potential of active chromium, but the oxidation temperature of 600°C. gave a potential which dropped to an active value of −0.62 v. in less than a minute. The maximum and minimum were obtained without exception for three different runs; but even so, the difficulty in extrapolating in the high temperature region leaves some room for doubt as to whether the curve actually bends down in this region or not.

Diffraction patterns of these samples for four of the temperatures in the range included in Fig. 2 are given in Fig. 3. The diffraction pattern for unheated chromium (Fig. 3a) was unchanged when the chromium was treated with nitric acid. All of the spots on this pattern were found to correspond to chromium in the body-centered cubic form. The orientation

is such that the 222 planes (Miller indices) are parallel to the outer deposited surface.

TABLE I. *Electron diffraction and electrode potential data on chromium*

Temperature of oxidation, °C	30	100	200	300	400	500	600
Appearance of surface	metallic lustre	same	same	same	same	yellow	blue
Diffraction pattern	oriented Cr	oriented Cr	oriented Cr, Cr_2O_3 (traces)	oriented Cr (traces) Cr_2O_3	oriented Cr_2O_3	oriented Cr_2O_3	less oriented Cr_2O_3
State of oxide	—	—	near amorph.	minute crystallites	small crystallites	crystallites	larger crystallites
Extrapolated potentials* HNO_3 treated	0.84	0.23	0.46	0.69	0.76	0.73	0.64
Air treated	0.18	0.21	0.32	0.50	0.54	0.63	0.60

* Volts with reference to saturated calomel electrode.

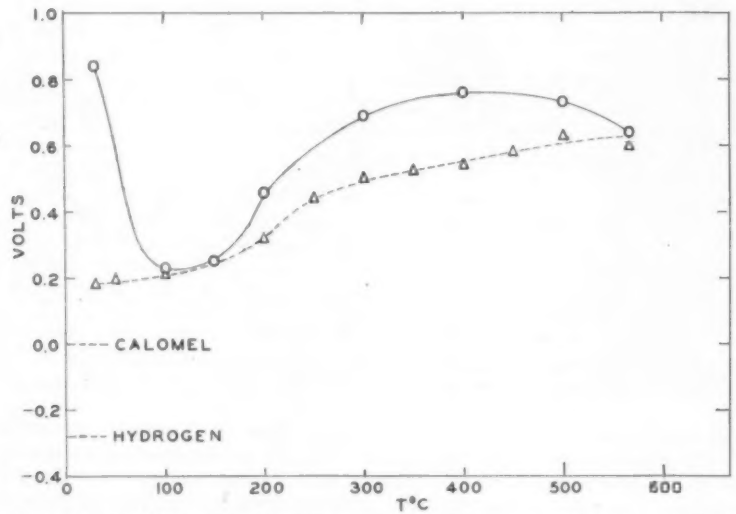

FIG. 2. Potential at time of immersion vs. temperature of oxidation. ——, HNO_3 treated. - - - - air treated.

In Fig. 3c the pattern is that of Cr_2O_3 in the hexagonal close-packed form. The chromium pattern is not evident here. Fig. 3b, however, shows a faint oxide pattern along with remains of the chromium pattern. The oxide pattern is not very distinct because the film is extremely thin and the crystallites are small. Fig. 3c indicates the presence of larger crystallites

due to the 450°C. heat treatment. The change in the diffraction pattern from 3c to 3d shows that the 650°C. treatment produces still larger crystallites and that the orientation has decreased considerably. The film first becomes visible with a faint yellow tint after one hour at approximately 450°C.

Comparing the diffraction data in Table I with the potential data, it is evident that the minimum in the curve occurs when no oxide is detectable. On the other hand the maximum occurs when the oxide is shown to be pres-

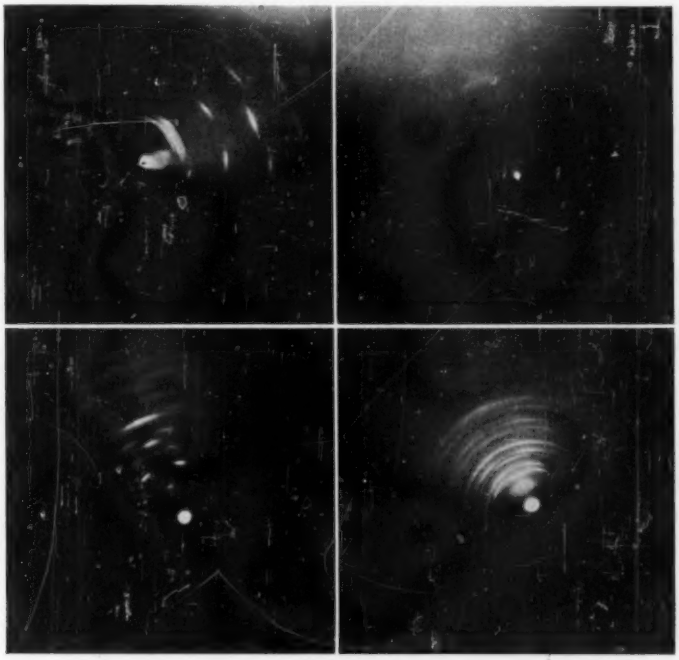

FIG. 3 a–d

FIG. 3. Electron diffraction patterns of chromium surfaces. a. No heat treatment. b. 1 hr. at 200°C. c. 1 hr. at 450°C. d. 1 hr. at 650°C.

ent by the diffraction pattern, although the film is not visible to the eye. There is no need to take this as evidence that the oxide is the fundamental cause of passivity since approximately the same potential was obtained with unheated chromium which showed no evidence of the oxide. A consideration of the time-potential curves (Fig. 1) leads to the suggestion that the extremely noble potential at zero time may be a property of the oxide itself and the potential corresponding to the true state of activity of the metal shows up only after the electrolyte has penetrated the oxide and reached the metal. This suggestion is based on the fact that the potential

decreases rapidly to a value corresponding to that of active chromium when the oxidation temperature is high.

A study of the length of time that it takes for the metal to reach a given active potential value would offer a better method for measuring the degree of passivity. An attempt was made to do this using such time-potential curves as those in Fig. 1. Results have not been satisfactory as yet, but indications are that the unheated chromium can remain passive for a number of days in saturated potassium chloride regardless of whether it was pretreated with nitric acid or not. Heated chromium, however, where the temperatures employed were higher than 400°C. becomes active in a very short time. Work is being continued along these lines.

CONCLUSIONS

Some conclusions concerning the role oxide films play in passivity of chromium may be summarized as follows:

Oxide films can appreciably alter the values of the measured electrode potentials of the metal surface.

The noble potentials obtained with oxide films on the metal need not be identified with passivity.

The metal can exhibit a noble potential even when no oxide can be detected on the surface.

The potential of chromium treated with nitric acid is more noble than that of the air-treated metal. This difference is greatest when the metal is not subsequently heated.

ACKNOWLEDGMENT

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CHROMATED PROTEIN FILMS FOR THE PROTECTION OF METALS[1]

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ABSTRACT

A process has been developed for protecting steel, zinc, aluminum, and brass from corrosion by the use of chromated protein films. Either casein, albumin, or gelatin is applied to the metal surface by dipping. The film is impregnated with chromate, which acts as an inhibitor of corrosion and hardens the film, by adding the salt to the protein solution or by a separate immersion. These films may be useful for the protection of certain metals in mildly corrosive atmospheres.

INTRODUCTION

The wartime scarcity of many non-ferrous metals led to the extensive substitution of plain carbon steel for copper, brass, aluminum, and stainless steel, both for military and civilian uses. The protection of the steel against corrosion, usually necessary for such uses, was generally obtained with zinc coatings. The tendency of the latter to form objectionable corrosion products in certain types of exposure led to a widespread use of chromate films on the zinc formed by chemical attack in aqueous chromate solutions. These were applied either by immersion, as in the Cronak and Iridite processes, or by electrolysis, as in the Schulein and Ano-zinc methods.

The chromate films formed on the surface of the zinc, though only a few hundred thousandths of an inch thick, inhibit corrosion of the zinc, probably through the presence of minute amounts of soluble chromate slowly liberated by the action of moisture. If this explanation is correct, it would seem feasible to enhance the corrosion resistance by applying a larger quantity of chromate to the metal surface. The proteins offer a good medium or vehicle for increasing the amount of chromate on the metal surface, as they are basic and readily absorb or combine with chromic acid.

Initially, the chromated proteins were studied to determine their usefulness for protecting zinc surfaces as substitutes for chemical surface treatments. Subsequently it was found that they were of value also for protecting other metals such as aluminum, steel and brass.

COMPOSITION AND APPLICATION OF PROTEIN FILMS

The principal constituents of the chromated protein films are: (1) a corrosion inhibitor for the metal, (2) a protein which acts as a vehicle for the inhibitor, (3) a hardening agent, and (4) a bactericide to prevent putrefaction of the protein.

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The proteins used in this investigation were gelatin, casein, and albumin, all three water soluble, and zein, which is insoluble in water but soluble in certain organic liquids such as ethyl alcohol.

Chromates may serve as three of the required constituents: the inhibitor, the hardening agent (especially on exposure to light), and the bactericide. The chromate ions may be introduced as chromic acid, a chromate, or a dichromate. Use of a chromate as a corrosion inhibitor is always necessary, but other materials, such as formaldehyde, tannins, or certain salts of the heavy metals can be used as the hardening agent.

The four functioning constituents of the film can be applied in a single step or in several steps, according to the compatibility of the agents and the degree of protection desired from the film.

In the "one-step" process, a coating mixture that contains the protein, a hardening agent, a protective chromate and bactericide is applied in a single operation. (A hardening agent which will not coagulate the protein must be used.) For example, chromic acid coagulates a gelatin solution but ammonium, zinc, or nickel dichromates do not. After being dried, such films should be exposed to light to decrease their solubility in water. Some gelatin solutions of this type are not stable, as they become thick and "ropey" on long standing. As another example, a casein solution may be treated with an ammoniacal solution of zinc chromate. On drying, the ammonia evaporates and the residual zinc chromate both hardens the film and serves as an inhibitor.

In the "two-step" process, which is usually the more satisfactory, the metal is first dipped into a protein solution. After the film is dry it is dipped into a chromate solution for one-half to three minutes, whereby the film is hardened and an inhibitor is incorporated. The film is then allowed to dry without being rinsed. The chromate solution contains chromic acid (0.5 to 2%) or a dichromate of zinc, iron, or nickel (1 to 10%). Longer periods of treatment or stronger concentrations of the hardening agent may cause disintegration of the protein film. Soluble dichromates of amines, such as diethylenetriamine and tetraethanol ammonium hydroxide, gave satisfactory protection but were not superior to the metal dichromates.

In the "three-step" process (a) a protein film is applied and dried, (b) is then hardened by any suitable agent such as formaldehyde, tannin, or chrome alum, and (c) is impregnated with a dichromate. This procedure is longer and does not offer any specific advantages in protecting metals.

In another variation of the process a paint, prepared by milling an insoluble chromate with a protein solution, was used. The articles are coated with this water paint, dried, and then hardened by treatment with an organic reagent or a dichromate. The pigment may be an insoluble chromate of zinc, barium, strontium, or of a lorol amine or hexadecylamine. Best results were obtained with a paint consisting of one part of casein, three of basic zinc chromate, and seven of water.

Emulsions of wax or rubber may be mixed with solutions of casein and zinc chromate to yield films for special applications that are apparently satisfactory though not superior in protective value to the unmodified films.

The method of preparing the protein solution is important because it varies to some extent with each protein. Gelatin is dissolved in water

with gentle heating. Albumin may be dissolved in water at room temperature by stirring, with or without the addition of 25 to 50 ml. of ammonium hydroxide per liter of solution. Casein is dispersed in water and brought into solution with the addition of 25 ml. of ammonium hydroxide per liter of solution.

The concentration and viscosity of the protein solution determine the thickness of the films produced by dipping. For most purposes, protein concentrations of about 10% are satisfactory. The solutions, especially of casein, become less viscous on standing for about a day. Protein solutions more concentrated than 20% by weight should be avoided because the thick films they produce crack on drying.

TABLE I. *Typical protein films*

Solution no.	Type	Composition	Application
		g/L	
1	Two-step	(a) Casein 100 NH_4OH (Sp. Gr. 0.90) 50 ml/L K_2CrO_4 2 (b) $ZnCr_2O_7$* 50	After dipping in (a), panels are dried, dipped two minutes in (b) and dried.
2	Two-step	(a) Egg albumin 100 NH_4OH (Sp. Gr. 0.90) 50 ml/L K_2CrO_4 2 (b) CrO_3 20	After dipping in (a), panels are dried, dipped for 30 seconds in (b) and dried.
3	One-step	Egg albumin 100 NH_4OH (Sp. Gr. 0.90) 50 ml/L $ZnCr_2O_7$† 20	After dipping, the panels are drained and dried.
4	One-step	Gelatin 100 $(NH_4)_2Cr_2O_7$ 30	Panels dried after dipping.

* $ZnCr_2O_7$ is not commercially available. A 30% solution can be prepared by slowly stirring a paste of 87 g. of ZnO in 200 ml. H_2O into a solution of 213 g. CrO_3 in 500 ml. H_2O.

† The $ZnCr_2O_7$ in the form of a 20 to 50% solution is treated with a minimum quantity of NH_4OH to redissolve the precipitate before adding this solution to the other components.

Typical compositions and steps involved in the preparation and application of the preferred protein films are summarized in Table I.

Proteins that are insoluble in water appear to have certain advantages over water-soluble proteins. The leaching of the film in humid atmospheres is slower and thus the effective life of the film will be longer. Zein, a product from corn, is a typical protein that is insoluble in water but is soluble in certain organic solvents. When this protein is impregnated with chromate, the film has a corrosion resistance comparable to, or better than that of the water-soluble proteins. However, these films are less practical than the water-soluble films because of the complexity of the organic zein solution. The required constituents of water insoluble protein solution include (1) the protein, such as zein, (2) an organic solvent, such as ethyl alcohol, (3) a stabilizer, such as formaldehyde, (4) a plasticizer, such as phthalate compounds, (5) a corrosion inhibitor, such as chromic acid, and

(6) a non-gelling component, such as an amine. The presence of the stabilizer is necessary to get the zein into solution in concentrations higher than 10%. Without the addition of a plasticizer, such as dimethylglycol phthalate, the films are very brittle and do not adhere to the metal. When the chromate is added to the zein solution, the protein gels within a short time unless amines are present.

A typical zein solution contains the following:

Zein	20 g.
Formaldehyde (40%)	15 ml.
Ethyl alcohol	100 ml.
Dimethylglycol phthalate	10 g.
Dimethylamine (30%)	5 ml.
Chromic acid	1 g.

This solution is more difficult to prepare than the aqueous protein solutions. While such films yield protection at least equal to that of water-soluble proteins, their use is too cumbersome to be recommended.

PROPERTIES OF THE FILMS

As previously noted, the thickness of the films produced by dipping depends principally on the concentration and viscosity of the protein solutions. Typical thicknesses obtained with 10% solutions that had been aged at least 24 hours were: for egg albumin, 0.00005 inch (0.00125 mm.) to 0.00015 inch (0.00375 mm.); for casein, 0.0001 inch (0.0025 mm.) to 0.0004 inch (0.01 mm.); and for gelatin, about 0.0002 inch (0.005 mm.). All these films were thicker than the proprietary chromate films which usually are not more than about 0.00003 inch (0.00075 mm.) thick.

When freshly prepared and hardened, the films are almost insoluble in water and are so hard that they cannot be scratched with the finger nail. Exposure to light further hardens some films and renders them still less soluble. However, special exposure to light is not necessary in most cases.

The chromated protein films are yellow and, unless opaque pigments have been added, are transparent. Their ductility and adhesion are sufficient to prevent cracking or separation when the metal is bent. Heating to 150°C. does not injure these films, whereas most chemically produced chromate films on zinc lose much of their protective value if heated to 100°C.

Protein films may be removed from the metal quickly by treating them with an alkaline solution, such as a warm 5% solution of sodium carbonate.

PROTECTIVE VALUE OF PROTEIN COATINGS

A. *General behavior*

The degree of protective value which chromated protein films will afford to metals can be inferred by consideration of their nature. The protein film without a chromate, even though hardened, is not impermeable to moisture and offers little protection against corrosion of metals coated with it. For example, steel or zinc coated with protein films which have been hardened in formaldehyde will corrode in the salt spray almost as quickly as uncoated metals. The protective value of the chromated protein coatings is derived almost entirely from the inhibiting action of the chro-

mate, and the effective life of these coatings depends on the length of time the chromate is retained. In an environment such as outdoor exposure, in which the chromate is readily leached out, the film will soon lose its protective value. On the other hand, the films give good protection to certain metals in the salt spray because the rate of leaching of the chromate is slow compared to the rapid corrosion of unprotected metals. These films have the most value in a sheltered environment, where corrosion is likely to occur either from condensation of moisture, as in storage, or from corrosive fumes, as in a chemical laboratory. For example, sheet steel

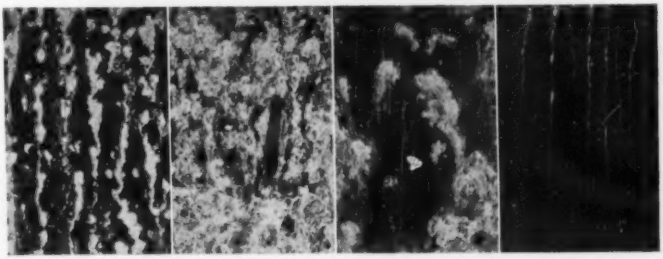


FIG. 1. Zinc plated steel panels after 14 days in salt spray. A. Oil. B. Chemical chromate. C. Chromated casein. D. Chromated egg albumin.

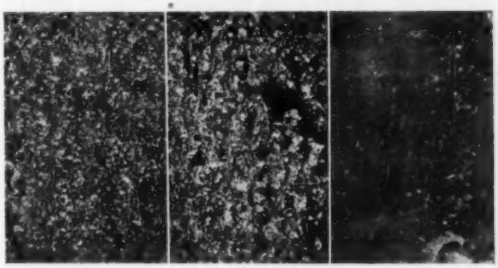


FIG. 2. Steel panels after 28 hours in salt spray. A. Oil. B. Phosphate. C. Chromated egg albumin.

rusts within a few days in a chemical laboratory, but remains bright for several months when coated with chromated protein.

The films protect zinc, steel, aluminum, and brass but have little or no protective value for magnesium or copper. In the following tests, specimens coated with chromated proteins were compared with those that had been coated with other accepted supplementary films, including inhibited oil, phosphate, chromate, and anodized films.

B. *Salt spray tests*

The chromated protein coatings as tested in the 20% salt spray gave better protection to zinc than chromate or phosphate films (Fig. 1). Steel panels coated with chromated protein showed slight rust after twenty-

four hours, while steel coated with an inhibited oil (U.S.A. Spec. No. 2-120) showed comparable rust in one hour and heavy rust after twenty-four hours (Fig. 2). After eleven days of exposure, aluminum coated with chromated protein was less corroded than aluminum that was coated by anodizing or by oiling (Fig. 3). Chromated protein films protected brass better than did oil or a nitrocellulose lacquer (Fig. 4). Copper and magnesium were not protected by chromated protein in salt spray tests.

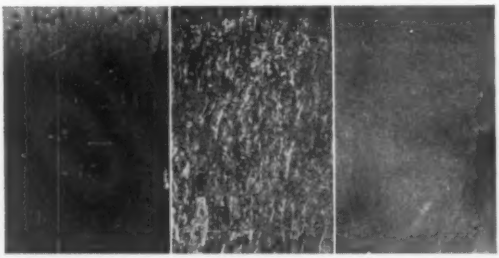


FIG. 3. Aluminum panels after 11 days in salt spray. A. Anodized. B. Oil. C. Chromated egg albumin.

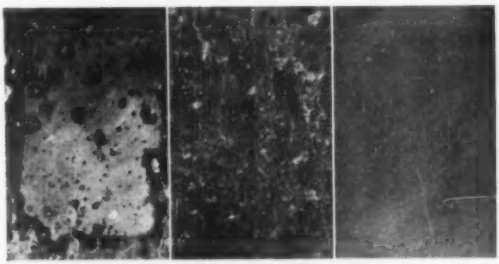


FIG. 4. Brass panels after 8 days in salt spray. A. Lacquer. B. Oil. C. Chromated egg albumin.

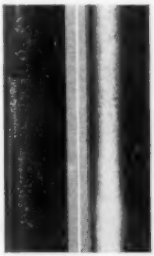
C. *Indoor exposure tests*

Zinc and aluminum panels exposed for one year in a chemical laboratory showed some tarnish, but not enough to differentiate between the chromated protein and other coatings. Brass and copper coated with chromated protein were not tarnished as much as were the oiled metals. Steel coated with oil or with a phosphate coating rusted in a few days, while that with a chromated protein was bright after six months (Fig. 5). Bare and anodized magnesium corroded more rapidly than when coated with certain chromated proteins.

D. *Outdoor exposure*

Some treated panels of each type of metal were exposed outside of a laboratory window in Washington, D. C. for several months. The steel

panels coated with protein held up better than panels treated with oil or phosphate; however, the difference was not as great as in the indoor exposures. There was not sufficient corrosion on the other metals (copper, brass, zinc, magnesium, and aluminum) to permit differentiation of the various supplementary finishes.



A. B.

FIG. 5. Steel rods after 4 weeks exposure in chemistry laboratory. A. Oil. B. Chromated egg albumin.

TABLE II. *Protective value of supplemental coatings on steel, plated with 0.00025" (0.00625 mm.) of zinc. Numerical ratings from 0 to 5, based on the extent of red rust at the end of the outdoor exposure and white corrosion at the end of the salt spray exposure period.*

Finish	Outdoor exposure					Salt spray
	Philadelphia, 2 years	Canal Zone 9 months		Washington, 4 yrs.	Average of 4 locations	5 days
		Marine	Jungle			
None	1.3	2	4	4.6	3.0	0
Chromate dip A	1.4	3	4	4.6	3.2	3.2
Chromate dip B	1.0	2	5	3.9	3.0	2.4
Chromate dip C	0.6	1	3	4.4	2.2	2.6
Chromate electrolytic A	0	1	4	4.1	2.3	3.6
Chromate electrolytic B	0.1	1	4	2.9	2.0	2.3
Chromate electrolytic C	0.1	1	3	3.6	1.9	0.3
Phosphate A	0.6	3	3	4.9	2.9	0
Phosphate B	1.3	3	4	4.7	3.2	0
Chromated protein	1.3	3	4	5.0	3.3	4.3

The most extensive outdoor tests were made on steel panels plated with 0.00025 inch (0.00625 mm.) of zinc, which were treated with nine different protective coatings and were exposed in Philadelphia, the Canal Zone, and Washington, D. C. The tests at Philadelphia and in the Canal Zone were made with the cooperation of Frankford Arsenal, for which we desire to express our appreciation. It should be noted that the location in Philadelphia represented a severe industrial exposure, and the location

in the marine part of the Canal Zone a severe marine exposure. The jungle atmosphere in Panama and the suburban atmosphere at the National Bureau of Standards were much less severe. Each panel was rated numerically on the following basis:

Rating	*Per cent of surface rusted*
5	0
4	0 to 5
3	5 to 10
2	10 to 20
1	20 to 50
0	over 50

The average scores in the four locations show superiority of the chromated protein over the other finishes. Most of the chromated zinc specimens, when subjected to long exposure in mild outdoor atmospheres, were inferior to uncoated zinc. The inferiority of the electrolytically chromated zinc to untreated zinc, especially in severe atmospheres, is no doubt caused by the fact that this treatment removed more of the zinc than did the chemical immersion methods of chromating.

Both the untreated zinc and the phosphated zinc, which had no chromate inhibitors, failed rapidly in the salt spray but gave fair service in mild outdoor and marine atmospheres. It will be noted from Table II that there are other specific cases in which the salt spray gave results contrary to the results of exposure in mild atmosphere. Hence the salt spray does not appear to be a satisfactory method for comparing the protective values of chromated zinc coatings in outdoor atmospheric exposure.

SUMMARY

The chromated protein coatings represent a cheap, expeditious means of protecting metals, especially zinc, iron, brass, and aluminum from corrosion during indoor exposure, for example, during storage. They are superior to direct phosphate or chromate coatings or to oil films for this purpose but their life is less than that of suitable paint coatings. The protein films are more effective on fairly large, regular surfaces than on the sharp edges and corners of small objects such as nuts and bolts where the film tends to pull away.

The protein solutions, unlike those used for direct phosphate or chromate treatments, do not become exhausted and require replenishment. After addition of the chromate the protein solutions are fairly stable for long periods. The same solutions and procedures can be used for several metals.

Metal surfaces must be entirely clean to ensure adhesion of the films. Plated articles may be taken from the plating bath, rinsed and coated without intermediate drying.

The protein films can be removed by treatment with warm sodium carbonate solution, a more convenient and less hazardous procedure than the removal of oil films with solvents.

RATE OF BREAKDOWN AND MECHANISM OF NITRITE INHIBITION OF STEEL CORROSION[1]

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ABSTRACT

A study was made of the effect of temperature and concentration on the breakdown of sodium nitrite in solution in the presence of steel. The end breakdown product of nitrite was identified and the effect of the ratio of cathodic and anodic areas on the consumption of nitrite was determined. The rate of consumption of nitrite was found to be dependent on the rate of steel corrosion. A mechanism of reduction of nitrite by adsorption at anodic areas followed by reduction of cathodic hydrogen to give an adherent protective oxide is proposed.

RATE OF BREAKDOWN AND MECHANISM OF NITRITE INHIBITION OF STEEL CORROSION

In a previous paper (1) on the inhibition of steel corrosion by sodium nitrite, the action of the nitrite was discussed from the point of view of weight loss as affected by temperature and rate of flow and these were correlated with potential measurements. A tentative mechanism of oxide formation was proposed. In this paper a more detailed investigation of the mechanism of inhibition and factors affecting the rate of consumption of sodium nitrite has been made.

W. Peters (2) investigated the decomposition of sodium nitrite in the presence of carbonic acid with various metals, including electrolytic iron. He concluded that it was the carbide in the iron which acted to reduce the nitrite. Baudisch (3) did a great deal of work on the reduction of nitrite by organic materials in the presence of iron salts and thought that the nitrite was reduced by first forming a complex with the iron salts. Neither of these mechanisms offers an acceptable explanation for nitrite inhibition of corrosion.

The breakdown of sodium nitrite was measured in the presence and absence of steel from 20°C. to 80°C. and for concentrations up to 100 p.p.m. Other tests include Static Immersion, Rocker, and Alternate Immersion tests, analyses for breakdown products and X-ray diffraction of the metal surfaces after test. The behavior of sodium nitrite in the presence of rust was also investigated. These have led to a fairly complete picture of the behavior of sodium nitrite as an inhibitor in aqueous solution.

APPARATUS AND METHODS

The breakdown tests were carried out in a covered four gallon (16 liter) glass jar equipped with a thermoregulator, heater, glass cooling coil, and

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Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

stirrer. A constant level device maintained the desired solution volume by additions of distilled water. The cover carried four lucite rods which supported the metal specimens in the solution. The alternate immersion and rocker immersion test equipment have been previously described (1, 7).

The panels used in these experiments were 4″ x 1″ (10 cm. x 2.5 cm.) low carbon, cold-rolled, 24 gauge steel. There was a ¼″ hole drilled near one end by means of which the panels could be suspended. These panels were first heat treated at 600°C. for one hour and then slowly cooled to room temperature in the oven. They were then descaled in 6N HCl containing 3% rhodine, washed in hot water followed by methanol, dried for ten minutes at 50°C. and finally weighed. At the conclusion of a run the panels, except where otherwise stated, were again pickled, washed, dried and weighed.

Analysis for sodium nitrite

The method is that described in "The Analysis of Water and Sewage" by Theroux, Eldridge and Mallmann (4), with some modifications which were found to give better results on the colorimeter. The final procedure adopted was as follows:

Reagents.

Sulfanilic acid. Dissolve about 8.0 g. of pure sulfanilic acid in 750 ml. of water and 250 ml. of glacial acetic acid.

Alpha-naphthylamine. Dissolve about 5.0 g. of alpha-naphthylamine in a mixture of 750 ml. of water and 250 ml. of glacial acetic acid. Filter through glass wool, store in a dark bottle equipped with a siphon and cover the solution with mineral oil.

Concentrated hydrochloric acid 12 N reagent grade.

The sample was placed in a 100 ml. volumetric and diluted to about 90 ml. with distilled water. Add 2 ml. of sulfanilic acid followed by 2 ml. of alpha-naphthylamine and 3 drops of concentrated hydrochloric acid and the solution then made up to 100 ml. After shaking, it was allowed to stand for fifty minutes and then read in the colorimeter. It was later found that standing at constant temperature (28°C.) gave best reproducibility. A green filter 540 mμ was used in the colorimeter.

For the purpose of standarizing the colorimeter a solution containing 100 p.p.m. sodium nitrite was prepared. From this the actual solutions used for standardization were prepared. The strongest solution read on the colorimeter contained about 1.6 p.p.m. sodium nitrite. At about 3 p.p.m. sodium nitrite a precipitate started to settle out after the solution had been allowed to stand for thirty minutes. In practice all samples were taken so that when diluted to 100 ml. they contained approximately one p.p.m. sodium nitrite or less. This standardization was checked periodically.

Analysis for dissolved oxygen

The method in use in this laboratory is the Winkler method described under the heading of Non-Referee Method C in an A.S.T.M. Preprint 1946 (5). Due to the presence of the nitrite it was necessary to modity it after the fashion of Rideal and Stewart (6).

PROCEDURE AND RESULTS

Constant temperature bath. Breakdown test

The procedure for starting a run was as follows: 16 liters of Ottawa tap water were placed in the bath and allowed to come to the desired temperature. After the water had reached the proper temperature, the required amount of sodium nitrite was weighed out, dissolved in about 100 ml. of distilled water and added to the bath. If panels were to be used these were placed in the bath immediately before the addition of the sodium nitrite. Approximately ten minutes from the time of its addition was allowed for the sodium nitrite to mix completely and then two samples were withdrawn, one for a sodium nitrite analysis and one for a pH reading.

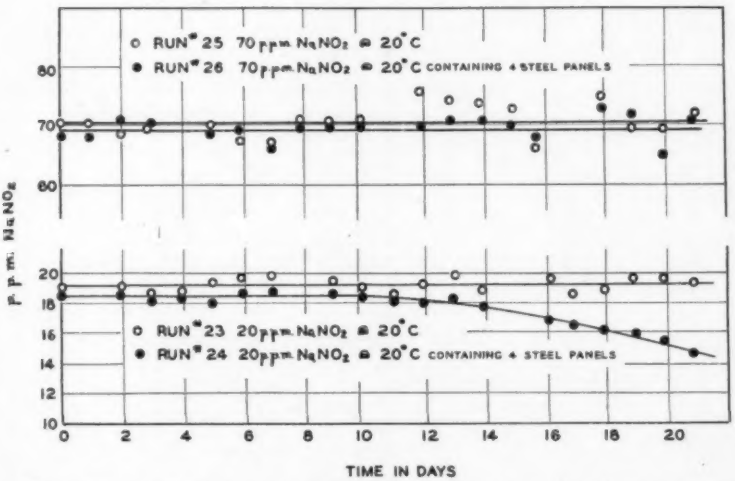
RUN# 25 70 ppm. NaNO2 @ 20°C
RUN# 26 70 ppm. NaNO2 @ 20°C CONTAINING 4 STEEL PANELS
RUN# 23 20 ppm. NaNO2 @ 20°C
RUN# 24 20 ppm. NaNO2 @ 20°C CONTAINING 4 STEEL PANELS
p.p.m. NaNO2
TIME IN DAYS

FIG. 1. Lack of breakdown of nitrite either alone or at fully nhibiting concentration. Slow breakdown at 20 p.p.m. at 20°C.

In the majority of tests samples were drawn daily for nitrite analysis and weekly for pH readings. The duration of the runs was three weeks except in those cases where the nitrite concentration was reduced to zero before that length of time; in which cases, the runs were cut when no further test for nitrite could be obtained. At the conclusion of a run, duplicate analyses for dissolved oxygen were carried out.

The tests were carried out in pairs, two runs containing the same amount of sodium nitrite and at the same temperature being started and stopped together. The only difference was that one run would contain four steel panels and the other none. In this way, it was felt that any breakdown of the nitrite evidenced was due to the presence of the steel and not to the effect of temperature.

The results obtained from these tests are shown as graphs in Fig. 1 to 5

inclusive. In these the effects of temperature, the concentration of sodium nitrite and the presence and absence of steel are adequately illustrated. In the absence of steel, no loss of sodium nitrite was observed in any case. As the temperature was lowered the concentration of sodium nitrite was kept constant and the temperature varied, a marked increase of corrosion occurred as the temperature rose. It is also significant that at those con-

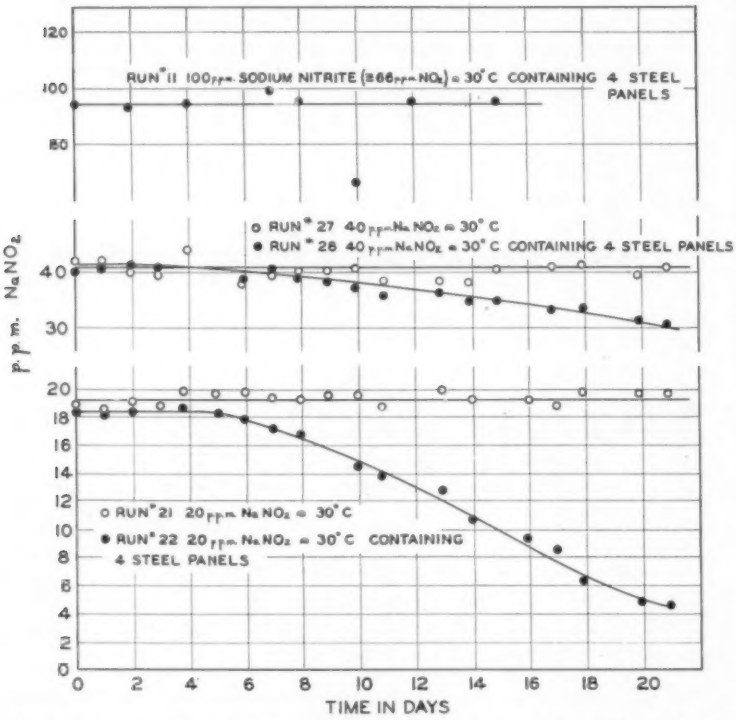
RUN # 11 100 p.p.m. SODIUM NITRITE (≡66 p.p.m. NO_2) ≈ 30° C CONTAINING 4 STEEL PANELS
o RUN # 27 40 p.p.m. $NaNO_2$ ≈ 30° C
• RUN # 28 40 p.p.m. $NaNO_2$ ≈ 30° C CONTAINING 4 STEEL PANELS
o RUN # 21 20 p.p.m. $NaNO_2$ ≈ 30° C
• RUN # 22 20 p.p.m. $NaNO_2$ ≈ 30° C CONTAINING 4 STEEL PANELS
p.p.m. $NaNO_2$
TIME IN DAYS

FIG. 2. Increase in rate of breakdown in presence of steel with lowered nitrite concentration. Temp. 30°C.

centrations which gave complete protection no loss of inhibitor could be detected.

No significant change in pH was observed either with or without panels; it remained in the vicinity of 7.0–8.0. In the dissolved oxygen tests, it was found that the oxygen concentration was higher in those baths containing no steel than in those containing corroding panels and it always remained slightly below saturation level.

When the panels had been completely protected, they appeared just as they had at the beginning of the run. No film or any other evidence of

their treatment could be discerned by eye. In most cases there was a very slight loss in weight of a few milligrams and in a few cases where the panels were washed and dried without being pickled, there was a slight but consistent gain in weight of a few tenths of a milligram. At concentrations

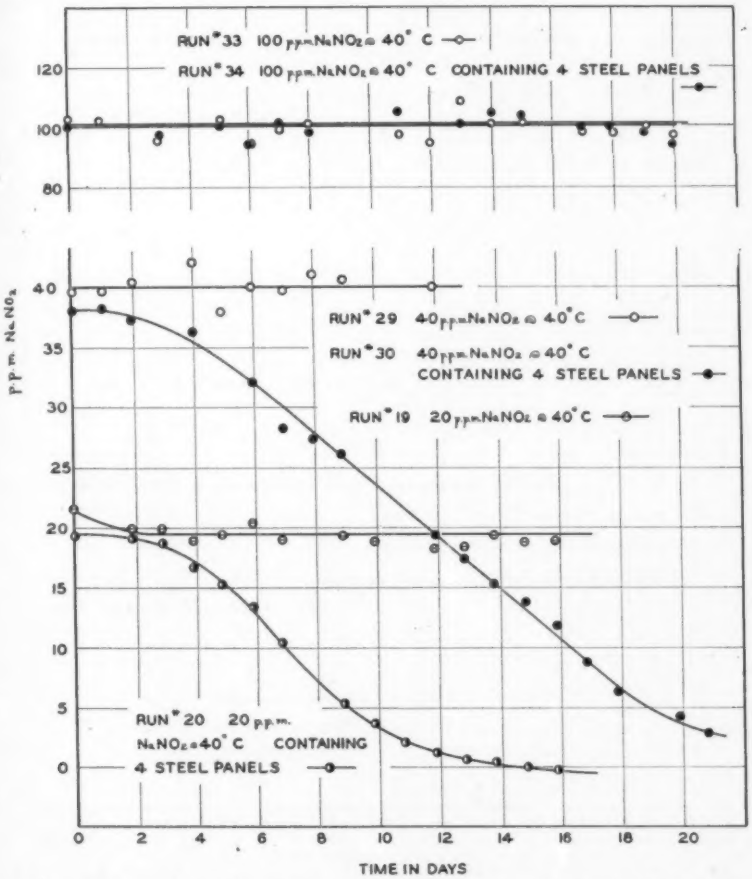

FIG. 3. Same as FIG. 2 at 40°C. Note slowing up as concentration diminishes.

slightly less than those required for complete inhibition, some areas of the panels were completely protected, other areas being covered with a powdery red rust. These concentrations of inhibitor gave the largest amount of loose red rust in the solution. Under this rust, after cleaning, fairly bad pitting was observed. At still lower concentrations the panels were completely covered with a loose rust, red on the outside and black next to the

panel itself. Here the pitting gave way to general attack; and the rust obtained in this region seemed to be more adherent as comparatively less was found in the liquid itself. Thus a more or less continuous variation of

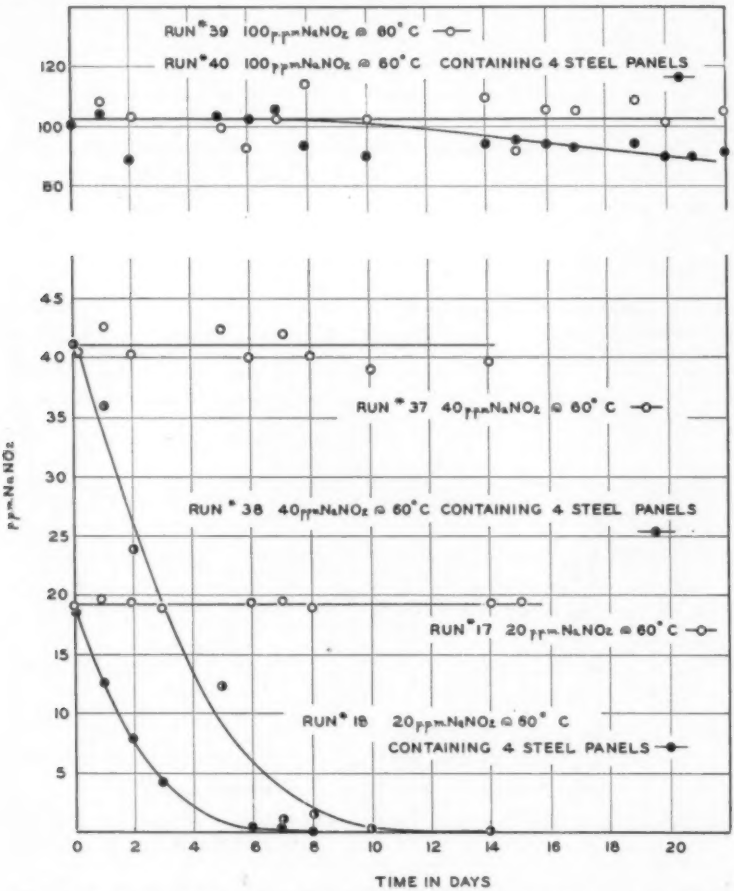

FIG. 4. Same at 60°C. Note higher concentration required for inhibition at higher temperature.

the type of corrosion could be followed as the nitrite concentration varied in any given direction.

Alternate, rocker, and static immersion tests

The method for setting up these tests is adequately described elsewhere (1, 7). In these tests, the concentration of sodium nitrite was varied from

10 p.p.m. to 100 p.p.m. One set of tests lasted seven days and another set lasted fourteen days. The panels from some of these tests were not cleaned but merely washed, dried and used as the subjects for X-ray

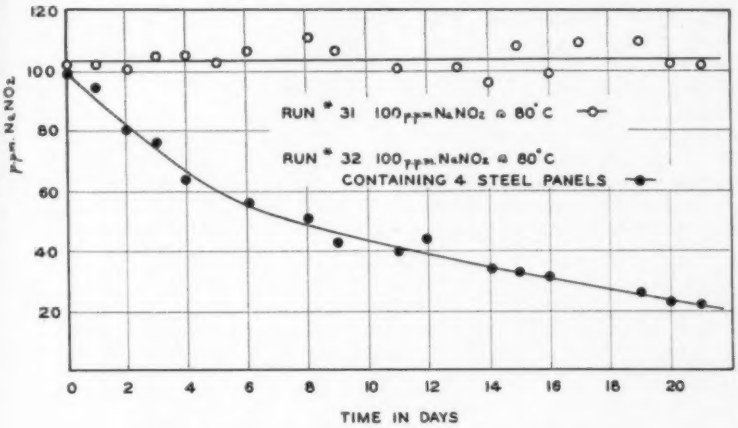

FIG. 5. Nitrite at 100 p.p.m. breaks down at 80°C.

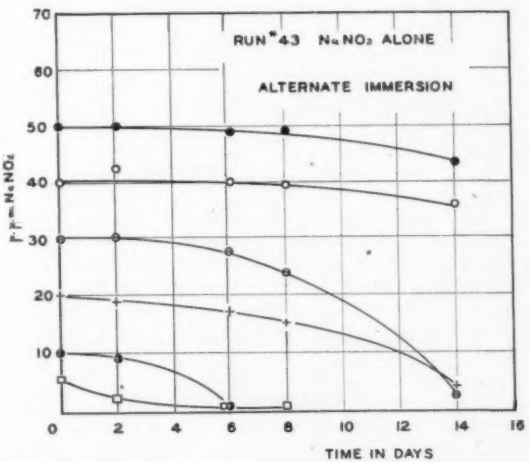

FIG. 6. Effect of concentration on rate of breakdown. Temperature 32°C.

diffraction pictures. For this purpose a Philips No. 3 circular camera, diameter 57.3 mm. and a back-reflection mounting were used. The radiation used was α-iron. As the concentration of sodium nitrite was varied in uniform steps, the panels represented fairly uniform steps from prac-

tically no inhibition to complete protection. In no case was there any evidence of sodium nitrite on the panels. The only substances which

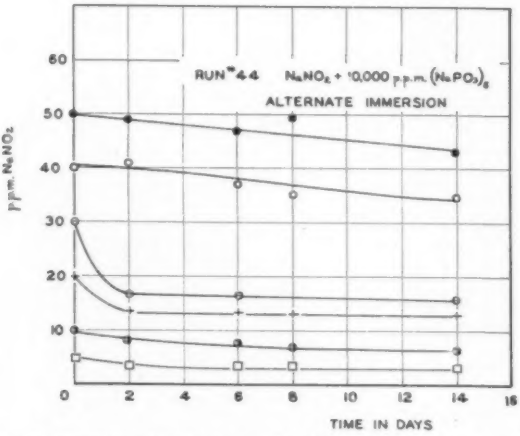

FIG. 7. Effect of complex phosphate on nitrite breakdown in presence of steel at 32°C.

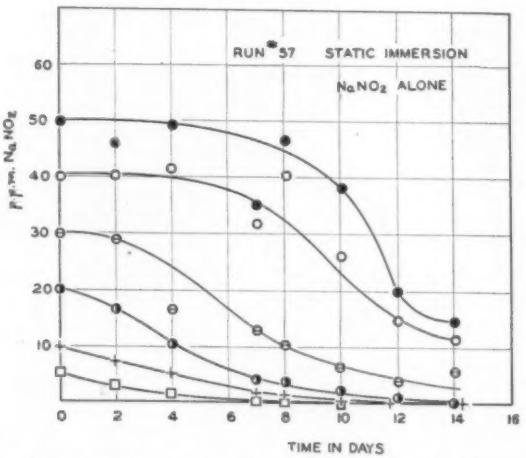

FIG. 8. Effect of concentration on rate of breakdown in static solutions at 32°C.

could be detected on any of the panels were any or all of the various oxides of iron.

Continuing the search for a reasonable mechanism, another series of tests on the Alternate Immersion machine was carried out. These were

run at sodium nitrite concentrations of 0, 5, 10, 20, 30, 40, 50 p.p.m. One set contained only sodium nitrite and Ottawa tap water and a second set contained sodium nitrite, Ottawa tap water, and 10,000 p.p.m. sodium hexametaphosphate (commercial glassy phosphate-calgon). The purpose of the calgon was to provide a continually fresh iron surface. In this way it was thought that the sodium nitrite would disappear faster in the presence of the calgon than in its absence. The results of these tests are shown in Fig. 6 and 7. At concentrations of five to ten p.p.m. sodium nitrite, the nitrite seemed to disappear faster when no calgon was present; but at the higher concentrations the rate of consumption was about the same. It is interesting to note that in the presence of calgon the sodium nitrite concentration does not fall completely to zero but seems to approach a small limiting value. In the absence of calgon the panels and the liquid both showed the usual amount of rust. In the presence of calgon the panels

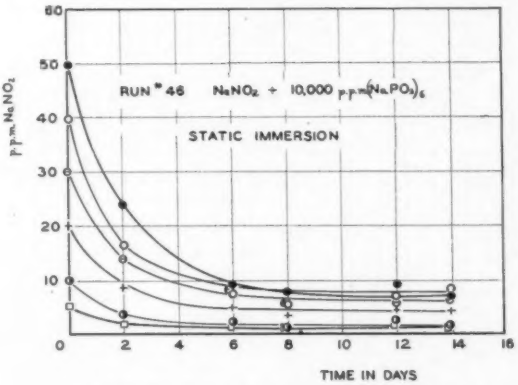

FIG. 9. Same as 8 with complex phosphate

showed indistinct interference tints, while the liquid remained clear with a tendency to turn yellow at the lower nitrite concentrations.

In conjunction with these, a similar set of Static Immersion tests were run. The results are shown in Fig. 8 and 9. This time in all cases the calgon accelerated the rate of breakdown of the sodium nitrite. Also the nitrite disappeared faster in these Static tests than in the corresponding Alternate Immersion tests. As before the panels and liquid in the absence of calgon showed the usual rusting. However, in the presence of calgon, while the panels remained clean and bright, the liquids took on a reddish-brown coloration which deepened as the sodium nitrite concentration increased. This was probably due to the iron held in solution by the calgon.

In both sets of tests weight losses were taken on all the panels. These are graphed for the Alternate Immersion method in Fig. 10 and for the Static Immersion method in Fig. 11.

Thus far no attempt had been made to discover the exact nature of possible breakdown products. Now the complete reduction of sodium nitrite brings about the production of ammonia, and hence, it was decided

to run a test which would enable us to determine if any ammonia was produced. The method used was as follows:

20 g. of fine, degreased, steel wool were refluxed in 500 ml. of a solution containing 1% sodium chloride, ½% sodium nitrite and 1 drop of concentrated sulphuric acid per liter for eight days. The temperature during

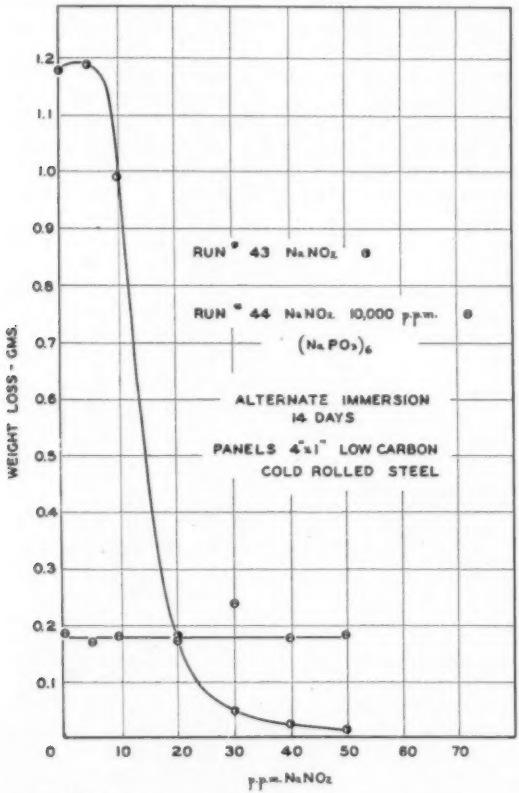

FIG. 10. Note lack of inhibition by nitrite in presence of complex phosphate in alternate immersion.

this time remained slightly above 100°C. At the end of this period, 5 g. of sodium hydroxide were added and the solution distilled over in 50 ml. lots until the flask was dry. Clean compressed air was then passed through the flask containing the steel wool and bubbled into 50 ml. of distilled water containing a few drops of concentrated sulphuric acid. The bubbling was continued until no further odour of ammonia could be detected from the flask or for about twenty minutes. Each 50 ml. lot was then quantitatively tested for ammonia with 2 ml. of Nessler's reagent, and diluted

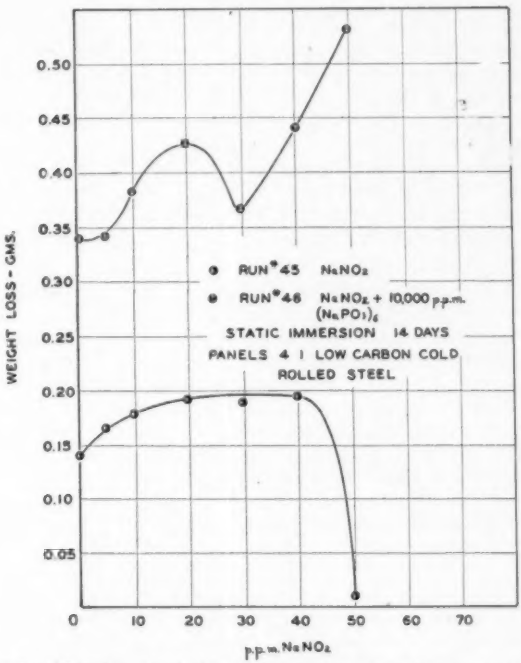

FIG. 11. Combination of nitrite and complex phosphate actually increases the rate of corrosion.

TABLE I

Run No.	Duration	Initial conc. $NaNO_2$	Final conc. $NaNO_2$	Temperature	Weight loss	Final pH	Dissolved O_2
	days	*p.p.m.*	*p.p.m.*	*°C.*	*grams*	*25°C.*	*p.p.m.*
26	21	70	70.0	20	0.0054	6.05	8.18
24	21	20	14.4	20	0.2146	7.64	7.44
11	17	94.2	94.2	30	−0.0005*	7.48	—
28	21	40	30.7	30	0.2058	7.87	6.55
22	21	20	4.5	30	0.6471	7.63	6.15
34	20	100	94.5	40	0.0033	7.92	5.49
30	21	40	3.2	40	1.1617	8.3	—
20	16	20	0.2	40	1.2063	7.98	4.29
42	19	100	91	50	0.0069	7.57	—
51	15	40	0.2	50	0.5026	8.4	5.85
49	9	20	0.08	50	1.7237	8.2	4.09
40	22	100	92.5	60	0.2422	8.01	3.65
38	14	40	0	60	1.7650	8.6	3.22
18	8	20	0.1	60	1.0811	8.81	—
32	21	100	22.0	80	1.0906	9.13	2.16

* Unpickled, washed in methanol.

when necessary. In all cases ammonia was found to be present; the following amounts were from three typical tests, 18.5 mg., 20.3 mg., 13.9 mg. At the completion of refluxing and before starting distillation, the liquid was tested for sodium nitrite. The tests showed that more than 70% of the sodium nitrite was found to have disappeared in all cases. Hence, approximately 3–4% of the sodium nitrite broken down was accounted for as ammonia, (Table II).

To determine the effect of rust alone on sodium nitrite, rust was made by alternate immersion of mild steel in Ottawa tap water for two weeks. This rust was transferred to new water and stirred with sodium nitrite at 35°C. Two concentrations of sodium nitrite, 17 p.p.m. and 50 p.p.m. were

TABLE II. *Rate of evolution of ammonia during distillation of solution remaining at end of eight days refluxing sodium nitrite, sodium chloride, and steel wool in Ottawa tap water*

Run No. 52A

Lot	NH_3	
	p.p.m. in sample	mg. in 50 cc.
1	11.2	0.56
2	1.6	0.08
3	0.3	0.02
4	—	—
5	—	—
6	0.5	0.02
7	9.5	0.48
8	65.0	3.25
9	312.0	15.60
*10	5.6	0.30
Total NH_3		20.31 mg.

* Lot 10 was obtained by blowing compressed air through the dry flask and bubbling it through 50 ml. distilled water containing 2 drops of conc. H_2SO_4 until no further odour of ammonia could be detected from the flask.

tried. No change in the concentration of the sodium nitrite could be detected within two weeks.

DISCUSSION

There are several facts which became evident on examination of Fig. 1–5. In the temperature range of 20°C. to 80°C. sodium nitrite is quite stable in Ottawa tap water. Also where the concentration of sodium nitrite is such as to give complete inhibition, the rate of breakdown in the presence of steel is not measurable in the time the tests were run. Consumption of the nitrite seems to occur only when the steel is corroding and the rate of breakdown is proportional to the rate of corrosion. This is evident from an examination of Table I and a comparison with the graphs. The concentration of nitrite required for inhibition increases with temperature, and in conjunction with this, the rate of nitrite consumption at any particular concentration below inhibition also increases with increasing temperature.

Weight loss measurements indicate that the nitrite at low concentrations can act as a stimulator of corrosion and this was taken to indicate that it acted in the same manner as a slight increase in oxygen concentration. That is, the nitrite can act to depolarize the cathodic areas by reacting with hydrogen. It has been shown that if a high oxygen concentration is present at the start and is maintained that under some conditions it will act as an inhibitor and under other conditions it will act as an accelerator of corrosion. For instance, Lee (8) found that increasing the oxygen concentration by raising the pressure increased the rate of corrosion of steel in N/10 potassium chloride solutions up to twenty-five atmospheres. These were stagnant solutions, which may account for the lack of inhibition at the higher oxygen concentrations. Addition of sodium nitrite is a simple way of increasing the oxidizing capacity of the solution and because of the much greater solubility of sodium nitrite than of oxygen in water, an oxidizing solution can be made which inhibits at least in Ottawa tap water and distilled water. A discussion of oxygen as both a stimulator and an inhibitor of corrosion is given by Evans (9).

There are two observations which seem to point to the mechanism of nitrite inhibition. First, there is no measurable consumption of nitrite without corrosion. Second, at concentrations slightly under those required for complete inhibition the corrosion takes the form of pitting. The latter fact indicates that the nitrite is suppressing anodic activity and this combined with the former observation indicates that nitrite breakdown occurs either at anodic areas or by reaction with corrosion products in the solution.

There are at least three possible reactions by which the nitrite may be reduced: by the hydrated ferrous oxide formed during corrosion; by the hydrogen formed on the cathodic areas; or by the bare iron at the anodic areas. (That reduction does take place is shown by the formation of ammonia in the experiments using steel wool.) There is no measurable oxidation by ferric oxide to account for consumption of nitrite under our conditions. The probability of direct reduction by iron is rather low. It was attempted to show this by the alternate immersion tests using 10,000 p.p.m. of sodium hexametaphosphate with the nitrite. This has a tendency to give a clean metal surface by its action of solubilizing iron oxide. At intermediate concentrations, after a short time, the rate of nitrite consumption fell off very considerably. In all cases the weight losses seemed to be independent of the nitrite concentration (Fig. 12). Without the phosphate, the consumption of nitrite was proportional to the weight loss. In static immersion the nitrite consumption was higher, probably because of depletion of phosphate at the metal surface but again had a tendency to fall to a constant level. In the case of static immersion the nitrite at the higher concentrations definitely stimulated corrosion in the presence of the phosphate.

It might therefore appear that where nitrite is being consumed rapidly the reaction is one between nitrite and ferrous compounds. However, this does not rule out a reaction with hydrogen and does not satisfactorily explain the anodic behavior of nitrite as an inhibitor. If it is assumed that the first step in nitrite inhibition is adsorption of nitrite at exposed iron atoms on an anodic area, and the second step reduction of this adsorbed nitrite by hydrogen at an adjacent cathodic area, a fairly satis-

factory picture of nitrite inhibition can be set up (see Fig. 12). This adsorption takes place by the linking of oxygen to iron atoms and it is the weakened nitrogen-oxygen linkage which is broken by the hydrogen. This type of mechanism will most easily explain the production of ammonia, but does not exclude the possibility that some of the nitrite is consumed by ferrous compounds when corrosion is taking place. The oxide film so formed must be quite protective but under ordinary conditions still soluble in sodium hexametaphosphate. The solubility in the phosphate, as indicated by continued corrosion, would appear to show that it is not adsorbed nitrite but oxide which is inhibiting corrosion. The tightly bound iron oxide is probably slightly soluble in water and the inhibiting nitrite

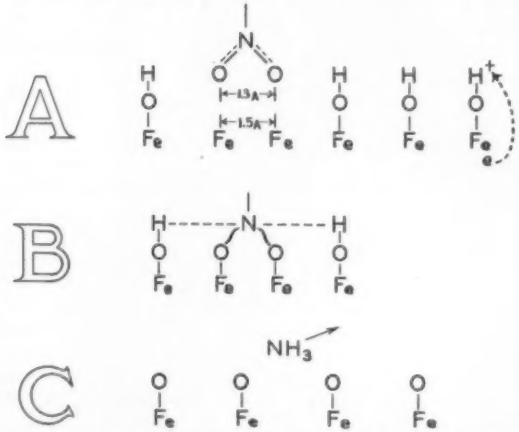

FIG. 12. Postulated mechanism for inhibition by nitrite. Nitrite ion is first adsorbed, then reacts with cathodic hydrogen to form reduction products and a continuous oxide layer.

concentration would be that which repaired the oxide film sufficiently rapidly as to keep metal loss below that which can be measured.

It should be noted that the inhibiting action of the nitrite is mainly due to the oxygen already present. The larger areas of oxide film are probably formed by air oxygen before immersion and later by oxygen in the solution. This does not form a completely protective oxide film and the nitrite acts to repair and complete the protective film. Thus, evidence has been obtained which shows that the nitrite will actually stimulate corrosion in oxygen-free solutions and its consumption starts at a higher rate in an oxygen-free solution than in oxygen containing water. If we assume that there is a definite percentage of the surface covered by oxide at any particular oxygen concentration then, all other things being equal, the nitrite required for completing the oxide film is dependent on the oxygen concentration. There is also the probability that the ease of formation of oxide by oxygen depends on the orientation of the crystal face exposed at the surface. There is a further possibility that the oxygen helps to precipitate

ferric hydroxide over the closely packed ferric oxide film and this contributes to a shielding effect.

In the case where the anodic areas form an appreciably large part of the total area, such as in the presence of the hexametaphosphate or in acid solution, the nitrite will act as a stimulator by its depolarizing action. Only when there is sufficient nitrite and oxygen to give a completely covered metal, i.e. when the metal surface is completely converted to cathodic type areas, will complete inhibition ensue. When there is insufficient nitrite to give complete coverage, corrosion will be localized and intensified by the nitrite stimulation of the cathodic reaction.

It is open to question whether the oxide film is present as chemisorbed oxygen or adsorbed iron oxide. Whichever term one chooses to use, it is evident that ferrous oxide with an intimate backing of iron and formed with the crystal structure of the iron lattice would behave differently from powdered iron oxide or ordinary hydrated ferrous oxide. For this reason the terms ferrous (or iron) oxide film and adsorbed iron oxide have been used.

The only reduction product of the nitrite which was isolated was ammonia. However, it is probable that other products are formed, such as nitrogen and nitrosyl compounds. In the steel wool experiments a large portion of the ammonia came off with first distillations, showing that some of the ammonia was in solution. With superheating at the end, more ammonia was released. This was probably tied up in a complex with some of the iron oxides or formed during the later almost dry heating.

Summarizing, it is felt that the mechanism of nitrite inhibition involves the following steps. Nitrite ion is adsorbed at the anodic areas. This weakens the nitrogen-oxygen bond sufficiently to allow reaction of the adsorbed nitrite with atomic hydrogen formed at adjacent cathodic areas. This results in the formation of an oxide layer contiguous with the surface and this oxide can be formed only at the surface. That is, this reaction does not occur with iron ions which have left the anodic areas. Due to the similarity of oxygen-to-oxygen distance in the nitrite ion to the iron-to-iron distance in the steel lattice, it may be that the nitrite ion is adsorbed at both oxygens, but that the stretching involved contributes to the weakening of the nitrogen-oxygen bond. It is also possible that the high concentration of nitrite required for inhibition is not only due to some solubility of the iron oxide, but mainly due to a probability factor which determines the adsorption of the nitrite either singly or doubly. At higher temperatures the increasing solubility of the oxide may require higher concentrations for inhibition.

This mechanism indicates that some nitrite will continue to be consumed as long as there are any appreciable anodic areas, but that the amount used will depend on the size of these areas, which in most cases also determines the rate of corrosion. That this is roughly true is shown from a study of Table I.

The presence of oxygen is desirable in that it promotes the formation of the initial oxide (cathodic) areas, so that the nitrite acts only to fill in. Some initial cathodic areas are helpful in supplying cathodic hydrogen for reduction of the nitrite.

The difference between nitrate ion and nitrite ion probably lies in either

the difference in the activation energies required for reduction or the difference in geometry or both. Chromate ion, on the other hand, probably does operate on a very similar principle to this. Some work on this is now going on in this laboratory. As a matter of fact, the role of oxidizing substances as inhibitors should be reconsidered on the basis of their geometry and ease of reduction to give FeO at anodic areas.

The fact that there is no measurable loss of nitrite when there is complete inhibition is due to the small amount of nitrite required to give a monomolecular layer of ferrous oxide, even taking slow repair into consideration. Although, on the basis of this argument, the main protective layer is FeO, a secondary protection may be obtained by a covering film of hydrated ferric oxide formed over and contiguous with this film by the highly oxidizing solution. However, where a sufficient concentration of nitrite is not present for complete inhibition, both oxygen and nitrite will contribute to corrosion. This accounts for the rise in the weight loss versus concentration curves at low concentrations and the only qualitative relation between corrosion and nitrite consumption in Table I.

From the practical point of view in a recirculation system, a high enough concentration of nitrite to give complete protection is the most economical in terms of total amount of nitrite consumed.

CONCLUSIONS

Sodium nitrite does not decompose in the absence of corroding steel.

The rate of consumption of sodium nitrite is dependent on the rate of corrosion.

The concentration of sodium nitrite required for inhibition increases with temperature.

Sodium nitrite is consumed by reduction.

The mechanism of inhibition which is proposed is that nitrite ion is adsorbed at anodic areas and reduced by adjacent cathodic hydrogen to give a continuous oxide layer which is protective. It is suggested that a mechanism of this type may be applicable to other oxidizing agents.

ACKNOWLEDGMENT

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AN ELECTROLYTIC THICKNESS TESTER FOR PLATED METAL COATINGS[1]

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ABSTRACT

A device is described which permits accurate measurement of the thickness of electrodeposited metal coatings. The principle of the instrument is the anodic dissolution of a defined area of the plated metal, using the current-time product as a measure of the thickness. The stripping current is held constant during a test and the removal time is automatically indicated. Successfully measured coatings include: tin, zinc, lead, cadmium, copper, chromium, silver, gold, and brass on steel; and tin, zinc, lead, and chromium on brass or copper. The accuracy is high; e.g., 30 micro-inches (0.76 micron) of tin on steel can be measured with an accuracy of plus or minus 2%.

INTRODUCTION

The principle of coulometric analysis has been applied to many chemical problems. It is the purpose of this paper to describe its application to the problem of measuring the weight (or thickness) of metallic coatings. While this has been done previously (1), the device discussed below has certain automatic features which make it particularly useful.

In order to apply coulometric principles to the determination of thickness of a plated metal coating, it is necessary that the following conditions be satisfied:

(a) It must be possible to dissolve anodically the metal coating more readily than the base metal (i.e., the coating must be anodic to the base metal in the electrolyte selected).

(b) The plated metal must be made to dissolve at 100% current efficiency (i.e., according to Faraday's law).

When these conditions are met, it is necessary only to know the following quantities in order to measure the coating thickness:

(c) The equivalent weight of the coating metal (when dissolved anodically in a given electrolyte at a given current density).

(d) The area of plated surface stripped.

(e) The density of the plated metal.

(f) The current used in stripping.

(g) The time required for stripping.

Factors (c), (d) and (e) are readily determinable. Items (f) and (g), however, are best measured in a particular way to facilitate ready calculations of the plating thickness. The quantity of metal stripped is, of course, proportional to the current-time product. If the current varies during the determination, the current-time curve must be integrated to permit

[1] Manuscript received December 18, 1947. Patent applied for.

Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

calculation of the plating weight. On the other hand, if the current is held at a constant value, the stripping time becomes a direct measure of the plating weight.

The device described below not only accomplishes this end, but also automatically records the stripping time. This is done by a vacuum tube relay, actuated by the voltage change which occurs at the anode of the stripping cell when the plated metal is completely dissolved. This voltage change always occurs when condition (a) is satisfied.

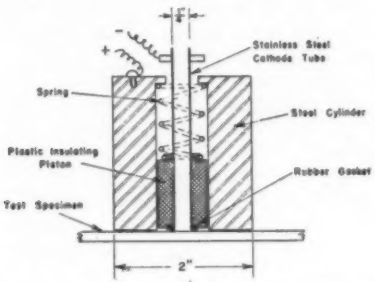

FIG. 1. Stripping cell for thickness tester

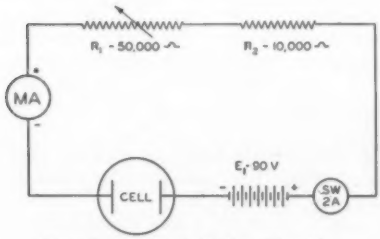

FIG. 2. Basic Stripping circuit

DESCRIPTION OF APPARATUS

Fig. 1 shows the design of the stripping head of the thickness tester. The weight of the external metal cylinder forces the piston against the plated surface of the test specimen. The rubber gasket provides a tight seal against leakage of the electrolyte. The center tube serves as the cathode of the cell, while the plated metal is the anode.

The basic circuit of the thickness tester is shown in Fig. 2. It will be noted that a 90 volt battery is used as the source of cell current, suitably regulated and metered by the other components. It is this feature which assures practically constant stripping current, since small voltage changes across the stripping cell are negligible compared to the 90 volt battery.

Fig. 3 shows the complete thickness tester circuit, including the vacuum tube relay, associated indicator lights, clock, etc. Battery E_1 furnishes current to the stripping circuit as well as to the relay circuit. Battery E_2 (with its voltage divider R_5) furnishes variable grid bias to the relay tube, thus permitting relay action to occur at any pre-selected value of

cell voltage, depending on the metal plating being measured. The dial scale of R_5 is calibrated to facilitate ready accommodation of the instrument to any of several plate-base metal combinations.

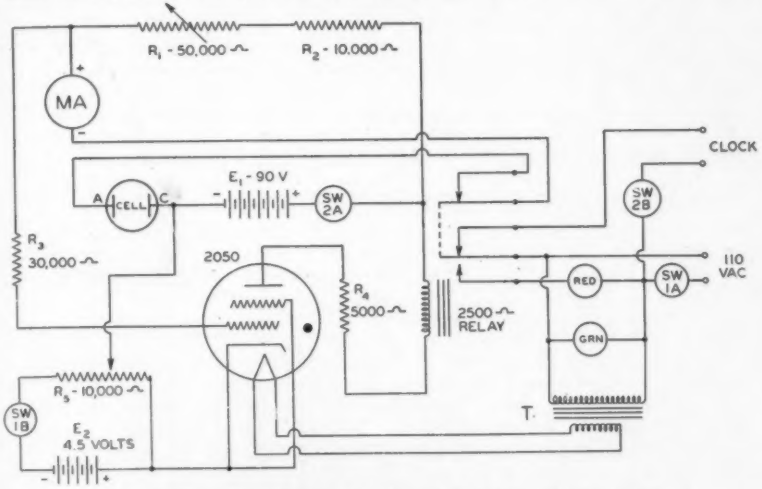

FIG. 3. Complete circuit of automatic plating weight tester

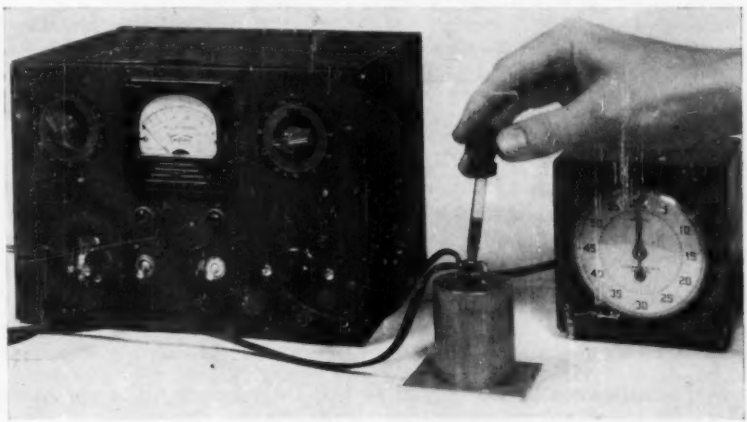

FIG. 4. Electrolytic plating weight tester

A photograph of the thickness tester in readiness for operation is shown in Fig. 4. The stripping head is designed to plug into the front panel to permit ready substitution of alternate cells for other types of plating measurements, e.g., wire, nuts, bolts, etc. The electric timer is similarly arranged to permit its use for other purposes.

OPERATION OF DEVICE

A brief description of the procedure used in making a typical thickness measurement will perhaps best illustrate the operation of the instrument. For example, in measuring the thickness of a sample of tinplated steel, the following steps are employed:

1. Switch 1A-1B is closed, preparing the instrument for operation.

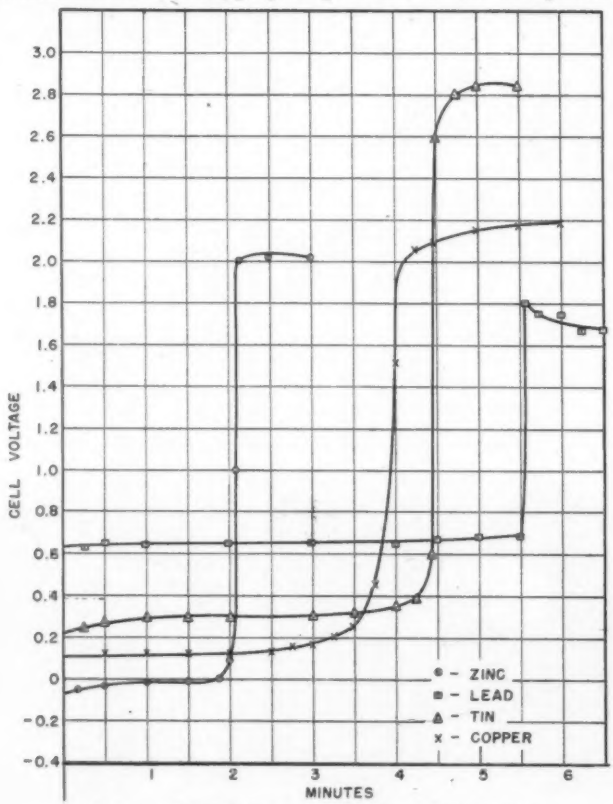

FIG. 5. Cell voltage vs. time for several metals

2. Potentiometer R_6 is adjusted so that relay action will occur at the sharp rise in cell voltage which occurs when the tin is removed (see Fig. 5, which shows several typical voltage-time curves).

3. The stripping cell is placed on the test specimen (Fig. 4), and the center tube is approximately $\frac{1}{3}$ filled with 10% sodium hydroxide using a small dropper.

4. Switch 2A-2B is closed, thus closing the stripping circuit while simultaneously starting the timer.

5. Resistor R_1 is adjusted to give 2 ma. stripping current, which is auto-

matically maintained during the test and need not be readjusted in subsequent measurements.

6. After a period of minutes during which the tin is dissolved (a 30 micro-inch (0.76 micron) coating requires two minutes), the relay operates, stopping the clock, opening the stripping circuit, and causing the red panel light to indicate completion of the test.

7. The stripping time is converted to plate thickness by one of two methods: (a) direct calculation from the current, time, area stripped, and equivalent weight of the metal, or (b) indirect calculation from the stripping time required for a standard thickness sample. Either method can be used to construct a table or graph of stripping time *vs.* plate thickness for each of several metals.

8. Switch 2A-2B is turned off, the electrolyte removed from the cell, and the cell rinsed with water. A piece of blotting paper may then be inserted between the cell and the specimen to absorb the remaining water. The apparatus is then ready for another test.

USES AND LIMITATIONS

The electrolytic thickness tester is particularly well suited to very thin coatings. Plating thicknesses from a few millionths of an inch up to several ten-thousandths have been measured quite satisfactorily. For coatings heavier than about 0.0005 inch (12.7 microns), however, the time required for stripping becomes rather long (30 minutes or more). While this time undoubtedly could be shortened by increasing the current (for some metals, at least), no detailed study of this possibility has been made. The maximum current density which could be used would be that at which the anodic efficiency dropped appreciably below 100%, and would not, therefore, be constant and independent of electrolyte concentration, temperature, etc. Other forms of plated materials can be tested as well as flat sheets.

Small plated parts, wire, etc. can be hung in a suitable cell, connected to the instrument, and deplated in a manner similar to flat surfaces.

Certain coatings, such as hot-dip or "melted" tinplate, hot-dip tin on copper, and lead-tin coatings on copper have an alloy layer between the coating and the base metal. These alloys are not measured by the thickness tester. Instead, only the "free metal" is determined. This "limitation" is useful, however, since combining the electrolytic method with a conventional chemical method allows estimation of the extent of alloying.

The electrolytes used for the coatings mentioned were 10% sodium hydroxide or 10% potassium cyanide, depending on the chemistry of the metals. The alkali soluble metals included tin, lead, zinc, and chromium, while the cyanide soluble metals were cadmium, copper, silver, gold, and brass. Silver and gold could not be determined on brass or copper, nor has a satisfactory electrolyte been found for nickel.

The applicability of the instrument to other metals has not been thoroughly investigated, nor have many electrolytes been studied.

Some interesting experiments have been performed on alloying rates between electroplated layers, using a vacuum tube voltmeter across the cell to indicate the relative solution potentials in different regions of the diffusion layer. Lead-tin and copper-tin diffusion have been studied in this way.

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THE ELECTROCHEMISTRY OF INDIUM[1]

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ABSTRACT

Recently revived interest in indium chemistry has demonstrated the importance of electrochemical studies and data. Available electrochemical information is useful in evaluating the ease of reduction of indium compounds, the ease of oxidation of the metal, the relative ionic characteristics of the compounds in the pure conditions and in solution, and the quantitative estimation of the element. The quantity production of indium metal in a high state of purity is based primarily upon knowledge of its electrochemical characteristics. Information summarized here is also strongly indicative of the necessity for further fundamental investigations.

INTRODUCTION

Although the discovery of indium was announced over eighty years ago (in 1863), comprehensive investigations of the characteristics of the element and its compounds have been limited, until quite recently, by the comparative scarcity of the element. Recent developments which have rendered the metal available in commercial quantities coupled with discoveries of desirable properties possessed by non-ferrous alloys containing indium have created new interest in this material. This is particularly true of its electrochemical characteristics, since much of the technical development has centered in electrodeposition. Although the literature contains much information about the deposition of the metal and about its fundamental electrochemical properties, the reports are widely scattered and completely uncorrelated. As a consequence, a detailed summation of available information seems appropriate.

ELECTRICAL CHARACTERISTICS OF INDIUM METAL

The electrical conductivity of indium metal is nearly the same as that of cadmium, being somewhat greater than those of the closely related metals gallium, tin, lead, and thallium but less than that of zinc. The specific resistance of metal of apparently high purity has been reported to be 8.37×10^{-6} ohm-cm. at 0°C. (1), 9.10×10^{-6} ohm-cm. at 23°C. (2), and 29×10^{-6} ohm-cm. at 155°C. (3) (liquid indium). The average temperature coefficient of resistivity between 0° and 100°C. has been given as 0.004904 for metal of extremely high purity (4). The decrease in resistance with increase in pressure has been measured over the pressure range from 0 to 12000 kg./cm.^{2} (4).

At extremely low temperatures, indium, in common with some of its

[1]Manuscript received December 29, 1947. This paper prepared for delivery before the Columbus, Ohio, Meeting, April 14 to 17, 1948.

close neighbors in the periodic system, becomes superconducting. The following data (5, 6) indicate disappearance of electrical resistance at 3.38°K.:

°K	81	20.6	4.2	3.38	3.37
ohm-cm. $\times 10^6$	2.15	0.537	0.322	0.317	0

Other more comprehensive data (7) give the same temperature for the threshold of superconductivity. Displacement of this temperature toward lower values with increasing pressure is slight.

Properties which measure the ease with which the indium atom loses electrons or the ease with which an ion of indium gains electrons have a direct bearing upon the electrochemical characteristics of indium and its compounds. The first four ionization potentials have been evaluated from spectroscopic data. Expressed in electron volts, these values are in order: removal of the *5p* electron from the neutral atom in its ground state $^2P_{\frac{1}{2}}$, 5.761 (8); removal of one *5s* electron from the In^+ ion in its ground state $^1S_0$, 18.79 (9); removal of the second *5s* electron from the In^{++} ion in its ground state $^2S_{\frac{1}{2}}$, 27.91 (10); and removal of a *4d* electron from the In^{+++} ion in its ground state $^1S_0$, 57.8 (11). Thus, oxidation states up to +3 may be expected, but higher states are precluded by the excessive amounts of energy required for their formation. Even the production of an In^{+++} ion is difficult, and one would expect indium (III) compounds to show extensive covalent bonding and but little true ionic character. This is, of course, in agreement with observed fact.

Qualitative and semi-quantitative measurements place indium slightly above tin or lead in the electromotive series but below iron and cadmium (12, 13). Exact potential measurements have been reported for chloride and sulfate solutions. From potentials observed at 25°C. for cells of the type

$$In(S)/InCl_3(m) + HCl\ (0.02f)/AgCl(S)/Ag(S)$$

in which the molal concentration m varied from 0.0015 to 0.0274, S. Hakomori (14) calculated the standard potential ($E°$) for the reaction

$$In(S) = In^{+++}\ (1m) + 3e^-$$

to be +0.336 v. (Latimer's convention) as referred to the molal hydrogen electrode. E. M. Hattox and T. DeVries (15), from potential measurements on cells of the type

$$In(S)/In_2(SO_4)_3(m)/Hg_2SO_4(S)/Hg(l)$$

obtained +0.340 v. (Latimer's convention) for the standard potential for the above reaction at 25°C. Their data also include standard potentials of 0.974 v. at 0°C., 0.962 v. at 15°C., and 0.946 v. at 35°C. for the cells of this type.

Comparison of the standard oxidation potential of indium with those for other metals, indicates that in contact with aqueous solutions, indium is about as easily oxidized as thallium (to + 1), somewhat more easily oxidized than cobalt and nickel, and somewhat less easily oxidized than cadmium and iron.

Experimental data for the oxidation of indium in alkaline solutions are lacking. From thermodynamic data for indium (III) oxide, W. Latimer (16) estimates the standard potential at 25°C. for the reaction

$$2In + 6OH^- = In_2O_3 + 3H_2O + 6e^-$$

to be +1.18 volt. This value is only approximate but corresponds with the values reported for the couples Ga − $H_2GaO_3^-$ and Cr–CrO_2^- and indicates indium to be reasonably easy to oxidize in alkaline media.

Latimer (16) also estimates that the standard potential for the reaction

$$In = In^+ + e^-$$

should be about +0.25 v., although this reaction is not observed because of the disproportionation of indium (I) to indium (III) and indium (0). Furthermore, for the reaction

$$In + Cl^- = InCl + e^-$$

the standard potential is estimated to be +0.34 v. (16). Comparative values for aluminum, gallium, indium, and thallium are of interest. These are recorded in Table I.

TABLE I.—*Standard oxidation potentials*

Acid solution		Alkaline solution	
Couple	$E°_{298}$	Couple	$E°_{298}$
$Al = Al^{+++} + 3e^-$	1.67	$Al + 4OH^- = H_2AlO_3^- + H_2O + 3e^-$	2.35
$Ga = Ga^{+++} + 3e^-$	0.52	$Ga + 4OH^- = H_2GaO_3^- + H_2O + 3e^-$	1.22
$In = In^{+++} + 3e^-$	0.34	$2In + 6OH^- = In_2O_3 + 3H_2O + 6e^-$	1.18
$Tl = Tl^{+++} + 3e^-$	−0.719		

Some single electrode potential data have been reported although they are not extensive and may be in error. Thus, Thiel (12) reported the following values (vs. the normal hydrogen electrode at 25°C.) for indium against indium chloride solutions of the indicted molar concentrations: 1M, + 0.094 v.; 0.1M, + 0.108 v.; and 0.01M, + 0.119 v. Downs and Kahlenberg (13) obtained the following potentials for cells including the normal calomel electrode (N.C.E.): N KOH, 1.115 v.; N Na_2SiO_3, 0.979 v.; N Na_2CO_3, 0.747 v.; N K_2CO_3, 0.543 v.; and 2N LiCl in pyridine, 0.503 v.

Polarographic reduction studies on indium (III) salt solutions have been summarized excellently by I. M. Kolthoff and J. J. Lingane (17). According to these authors, reduction of the aquo indium (III) ion is extremely irreversible and proceeds only at a high overvoltage. The half-wave potential of the perchlorate in 0.1N perchloric acid solution is −0.95 v. (vs. the saturated calomel electrode, S.C.E.), but the addition of the chloride ion shifts the wave toward more positive potentials[2] and renders it better defined, possibly because of chloroindate (III) ion formation. In 0.1 N

[2]The signs on polarographic potentials in keeping with the convention of Kolthoff and Lingane, are the exact opposites of those used above for oxidation potentials. This difference should be recognized throughout the discussion to avoid confusion.

and 1 N potassium chloride solution, Kolthoff and Lingane find half-wave potentials of −0.561 and −0.597 v. (vs. S.C.E.) respectively. In potassium chloride medium, reduction is reversible and corresponds to the addition of three electrons.

Polarographic studies on indium compounds date from the pioneer work of J. Heyrovsky (18) on indium (III) chloride solutions of several concentrations. Half-wave potentials (vs. N.C.E.) of −0.63 and −1.13 v. for reduction of indium (III) in neutral or weakly alkaline solution and in 1N alkali, respectively, have been reported (19). J. Tomeš (20) obtained a corresponding value of −0.636 v. The normal deposition potential of −0.500 v. (vs. N.C.E.) from 0.1 N hydrochloric acid solutions (21) is of importance in permitting the polarographic estimation of indium in the presence of zinc or gallium.

A hydrogen overvoltage of 0.533 ± 0.007 v. has been reported (22) for indium in 2N sulfuric acid solution at 25°C. This compares with a value of 0.570 ± 0.003 v. given for mercury under comparable conditions and accounts for the difficulty experienced in dissolving indium in non-oxidizing acids.

ELECTRODEPOSITION OF INDIUM METAL

Data just considered indicate that indium should be comparatively easy to deposit electrolytically from aqueous solutions of its compounds. Since the first deposition experiments carried out by L. Schucht (23), many procedures have been proposed. From purely academic effort, interest has shifted in recent years toward quantity production of metal of high purity and toward plating other metal surfaces. Baths suggested for the electrodeposition of indium may be classified roughly as those containing simple indium (III) compounds, those containing added organic compounds, and those containing added cyanide.

Baths containing simple indium (III) compounds

Deposition from indium sulfate solutions was first reported by Schucht (23). Thiel employed the same procedure in his early studies (24) and reported quantitative deposition of the metal on a platinum cathode in either the presence or absence of ammonium sulfate. Deposition from sulfate baths containing some free sulfuric or acetic acid and gelatine is also said to be quantitative (25).

Extensive studies on sulfate baths have been reported by C. G. Fink and R. H. Lester (26). According to these authors, addition of boric acid reduces crystal size in the deposit and increases current efficiency, whereas addition of both boric acid and sodium hydroxide reduces the quality of the deposit and causes current efficiency to pass through a minimum. Best deposits were obtained when aluminum sulfate and gelatine were present, with baths being 0.1M in indium (III) oxide, 0.3 M in sulfuric acid, 0.0173 M in aluminum sulfate, and containing about 0.0075 g. of gelatine per liter being recommended.

For technical electrodeposition, the acidic sulfate bath proposed by H. B. Linford (27, 28) has given very favorable results. This bath contains some 20 g. of indium as sulfate per liter, some 10 g. of sodium sulfate per liter, and sufficient sulfuric acid to maintain the pH at around 2.0. Care-

ful pH control over the range 2.0–2.7 is essential. The indium content of the bath is maintained and pH control effected by the use of combined indium (soluble) and iron (insoluble) anodes. Baths are operated at room temperatures and are stable for periods of many months. Current efficiency is high, and deposits are smooth and adherent. In the opinion of certain authors (29, 30, 31) the acid sulfate bath is cheaper and easier to prepare than the cyanide bath but more difficult to operate and control.

The sulfamate bath has received attention recently. According to Murray (32), these baths are the best developed thus far. They are reported to operate at 90% cathode efficiency and 100% anode efficiency. They are clear and stable and have excellent throwing power. Furthermore, they are inexpensive. An indium content of some 20 g. per liter as sulfamate is suggested (32).

Deposition from fluoborate, fluosilicate, and fluoride baths has been covered by patent (33). The fluoborate bath has been most extensively investigated of these three. According to Murray (32), the bath is expensive because 25–100 grams of indium per liter are required. Operation in the pH range 0–0.2 and at cathode efficiencies of around 40% are reported (32). On the other hand, fluoborate baths with excellent throwing power and cathode efficiencies around 75% have been described (34). Such baths are recommended to contain 72 g. of indium as fluoborate per liter, 22–30 g. of boric acid per liter, 40–50 g. of ammonium fluoborate per liter, and sufficient fluoboric acid to maintain the pH at 1. Soluble anodes of indium may be employed, although bagged carbon or platinum is recommended.

Deposition from simple chloride solutions containing little free hydrochloric acid was used by F. C. Mathers (35) to purify indium metal. The same general procedure has been employed more recently for recovery of metal of high purity for atomic weight (36) and electrochemical (15) studies. Baths containing simple indium salts and large quantities of free sodium hydroxide have been used (31), but usually some precipitation inhibitor such as glucose is necessary.

Baths containing added organic materials

Schucht (23) deposited indium from salt solutions containing various organic acids. Satisfactory deposits have been obtained from chloride, nitrate, or sulfate solutions in the presence of pyridine (37) but not in the presence of oxalic acid or acetic acid. Best results were obtained, however, when indium sulfate solutions were treated with formic acid and ammonia prior to electrolysis (37). Such solutions yielded compact, crystalline deposits. Use of formate and oxalate solutions for quantitative electrodeposition will be discussed in a later section.

Baths containing tartrate work well. Kollock and Smith (25) obtained best results with a mercury cathode from sulfate solutions containing Rochelle salt. Use of an alkaline bath containing tartrate and ammonia has been covered by patent (38) as has use of baths containing formate, oxalate, or tartrate (39). A cyanide-free alkaline bath containing dextrose has also been patented (40), but use of baths of these types, except the tartrate (31), has been quite limited.

As a result of detailed studies on the electrodeposition of indium, L. R. Westbrook (40) concluded that a bath prepared by dissolving 200 g. of indium (III) oxide in 600 ml. of solution containing 120 ml. of 96% sulfuric acid, adding 250 g. of sodium citrate crystals, and diluting to one liter is superior to simple salt and cyanide baths in that it is stable, gives compact, thick deposits, and may be stripped completely of its indium content. Electrolysis is effected at room temperature with platinum anodes and steel or indium cathodes. Indium of high purity has been obtained by this means (42, 43).

Baths containing added cyanide

Cyanide baths were the first to be used for the commercial electrodeposition of indium and are still among the most generally useful. Early efforts toward use of cyanide were complicated by hydrolytic precipitation of hydrous indium hydroxide from such media. In 1932, D. Gray (44) effected stabilization of cyanide baths through addition of glycine and other organic compounds. Later, glucose (dextrose) was found to be equally effective (45), and a comprehensive study reported in 1934 (46) showed that satin-like, soft, silvery deposits of indium could be obtained over wide current density ranges from baths containing 30–50 g. of indium per liter, excess sodium cyanide, and about 0.5 g. of glucose per gram of indium. Such baths were stable toward precipitation, but although cathodic efficiency approached 100% when the baths were first prepared, it dropped rapidly to around 50%. Insoluble anodes of platinum or graphite were preferred to soluble ones of indium because of hydroxide formation on the latter.

The compositions and properties of Gray's original cyanide baths characterize recently described baths based upon his work (47, 48). Such baths are commonly prepared from technically available indium (III) chloride solutions and are operated at room temperatures (29, 30). Because of the use of insoluble anodes, constant replacement of indium by addition of its chloride is necessary. Other disadvantages (29, 30, 49, 50) are: necessity for aging of bath prior to use, tediousness of preparation, constant deposition of black, indium-containing residues, and costliness of components. Bath control is easier than with the acid sulfate medium, however.

Difficulties of preparation, aging, and decomposition are said to be overcome by raising the pH to around 11 by addition of sodium or potassium hydroxide (49, 50). Baths containing 15–30 g. of indium, 140–160 g. of potassium cyanide, 30–40 g. of potassium hydroxide, and 20–30 g. of glucose per liter are reported to yield white deposits of the metal even down to low indium concentrations at satisfactory cathode efficiencies and with great stabilities.

Electrodeposition is important not only for the preparation of indium metal of high purity and its concentration from salt solutions but also for the application of corrosion resistant plates. Indium is deposited best on non-ferrous metal bases. Its application to ferrous metals must be preceded by deposition of other non-ferrous coatings such as zinc, cadmium, or copper. Electrodeposition is also important as an analytical method.

ELECTROCHEMICAL PROPERTIES OF INDIUM COMPOUNDS

The electrical conductivities of a few anhydrous indium compounds have been reported. Thus, the conductivity of indium (III) oxide varies from 10^{-5} to 10^{-3} reciprocal ohm per centimeter in the temperature range 20–300°C. (51). Corresponding values for indium (II) oxide are 1×10^{-3} to 3×10^{-1} reciprocal ohm.

The equivalent conductance of fused indium (I) chloride varies from 39.2 to 70.1 reciprocal ohms over the temperature range 242–351°C. (52, 53) and follows the relation

$$\Lambda = 33.4 + 0.29\ (t - 225).$$

A value of 33.4 reciprocal ohms is then calculated at the melting point (225°C.). In its conductance this chloride of indium resembles the chlorides of monovalent silver, copper, mercury, and thallium. The equivalent conductance of fused indium (II) chloride is somewhat lower and varies from 15.3 to 25.6 reciprocal ohms in the temperature range 356–507°C. (51). The relation

$$\Lambda = 6.9 + 0.07\ (t - 235)$$

applies, and the value at the melting point (235°C.) is then 6.9 reciprocal ohms.

Conductance studies on fused indium (III) halides are more extensive. Experimentally determined values for equivalent conductance agree closely with those calculated from the following expressions: (52, 53).

$$\begin{aligned} &\text{For } InCl_3\text{: } \Lambda = 14.7 - 0.017\ (t - 586) \\ &\text{For } InBr_3\text{: } \Lambda = 6.4 - 0.001\ (t - 436) \\ &\text{For } InI_3\text{: } \Lambda = 2.3 + 0.013\ (t - 210) \end{aligned}$$

From these equations, values (in reciprocal ohms) at the melting points are, respectively: $InCl_3$, 14.7; $InBr_3$, 6.4; and InI_3, 2.3. Thus, increase in covalent character parallels increase in size of halide group. Increases in equivalent conductances of halides at the melting points in the series boron, aluminum, gallium (III), and indium (III) for a given halogen (54) indicate the indium compounds to be the most ionic.

The conductivities of solutions of indium (III) chloride in acetone have been measured (55). Solutions containing 26% indium chloride by weight have maximum conductivity, and conductivity increases linearly with temperature in the range 5–40°C. Electrolysis of such solutions yielded shiny, dense deposits of indium at 100% cathode efficiency.

Conductivity studies on aqueous indium (III) halide solutions indicate weak electrolyte behavior, probably because of halo-complex ion formation. Values reported for equivalent conductances (Λ) at 25°C. for chloride (12) and at 18°C. for bromide (56) solutions are summarized in Table II. Values for bromide solutions are smaller than those found for strontium and chromium (III) bromide solutions of the same concentrations but only slightly larger than those measured for highly complexed cadmium bromide solutions. Values for chloride solutions approach those for the bromide quite closely.

Various studies relating indirectly to the electrochemical properties of indium compounds have been reported. Among these may be mentioned

the evaluation of activity coefficients of indium (III) sulfate solutions (15), evaluation of hydrolysis constants for sulfate (15) and halide (57, 58) solutions, and potentiometric studies on the precipitation of the hydrous hydroxide with ammonia and alkalies (59, 60, 61) and with chromate (62). Since these studies concern electrochemical methods more directly than electrochemical properties, they need not be described here.

Polarographic characteristics of indium (III) compounds have been described in discussions relative to the metal itself.

ELECTROCHEMICAL METHODS OF ANALYSIS

The pioneer investigations of Thiel (24) showed the feasibility of quantitative estimation of indium by electrodeposition as the metal. Kollock and Smith (25) reported quantitative results with both mercury and platinum cathodes and recommended solutions containing Rochelle salt as giving best results.

Estimation of indium on a microscale by deposition from solutions containing oxalate and made basic to methyl orange with aqueous ammonia

TABLE II.—*Conductance data for indium (III) halide solutions*

$InCl_3$		$InBr_3$	
Concentration	A	Concentration	A
equiv./liter	*reciprocal ohms*	*equiv./liter*	*reciprocal ohms*
3.0	10.2	3.7875	11.04
0.3	30.5	1.9986	19.83
0.03	50.6	1.0038	28.67
0.003	101	0.4992	37.02
0.0003	225	0.2000	46.75
		0.1003	53.85

has been reported to give derivations ranging from 10 parts per thousand with 2 mg. samples when solutions were measured volumetrically to 2 parts per thousand with 0.4 mg. samples when weight burettes were used (63). Electrolysis for 30 minutes at 3 v. and at 70–80°C. with platinum electrodes is recommended. The oxalate electrolyte gave the best results of a number investigated.

Accuracy within 0.1% has been reported for electrolytic determination of indium in 50–100 mg. quantities from formate solutions containing borax (64). Evaporation of sulfate solutions to dryness and mild ignition to remove free acid is followed by dissolution of the residue and addition of borax and sodium formate. After sufficient formic acid is added to dissolve the precipitate, electrolysis is effected at 0.2–0.25 amp. with a copper coated platinum cathode and a spiral platinum anode.

Internal electrolysis has been employed for the accurate estimation of 1–50 mg. of indium in sulfate or chloride solutions containing added sulfuric or hydrochloric acid, Rochelle salt, and ammonium chloride (65). The solutions are heated to 70–75°C., and internal electrolysis is effected with zinc anodes and weighed platinum cathodes. Optimum results are obtained at pH 3.5–3.8. Indium may be so determined in the presence of zinc in chloride medium, as well as in the presence of other common qualita-

tive group III metals. Iron interferes only when present in amounts greater than 150 mg.

Polarographic estimation of traces of indium in certain other metals was first reported in 1925 (66), an accuracy of 10% in 10^{-5} N solutions being attained together with detection of a little as 0.0001% of indium in zinc. The measurements of Takagi (21) showed that indium can be determined polarographically down to a minimum concentration of 10^{-5} mole per liter in the presence of either zinc or gallium. The gallium and zinc waves are approximately 0.5 and 0.4 v. more negative, respectively, than the indium wave.

Polarographic estimation of small amounts of indium in the presence of iron is possible if prior reduction of the latter to the ferrous condition is effected with hydroxylamine hydrochloride (67). Determinations in the presence of cadmium are complicated by coincidence of the polarographic reduction waves for indium and cadmium at −0.63 v. (vs. N.C.E.). For estimation of indium in zinc blendes in the presence of cadmium, two polarograms are obtained (68). The first, in 0.1 M potassium chloride-hydrochloric acid solution, gives the sum of the indium and cadmium contents and the second, in N ammonia which is 0.002 N in ammonium chloride and contains agar plus a crystal of sodium sulfite, gives only the cadmium content because of precipitation of the indium. Acceptable results are obtained if the ratio of cadmium to indium is less than five to one. The polarographic method has been employed successfully for estimation of amounts of indium down to 0.5 mg. per 100 ml. in solutions containing dextrose and hydrochloric acid (69).

Only one potentiometric titration procedure has been proposed. Accuracy of 0.1–0.2% is reported when indium (III) chloride solutions are titrated with potassium ferrocyanide and the end point determined potentiometrically (70). The precipitate obtained corresponds in composition to $K\ In_5\ [Fe(CN)_6]_4$. This procedure has been applied successfully to the estimation of indium in alloys (71).

Any discussion of this paper will appear in the discussion section of Volume 93 of the Transactions of this Society.

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